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FINAL REPORT

DEMAND GAS GENERATOR

TECHNOLOGY PROGRAM (U)

Contract No. F04611-70-C-0024

Prepared by:

George F. Kirchoff

NORTHROP CAROLINA, INC.
A Subsidiary of Northrop Corporation
P. O. Box 3049
Asheville, North Carolina 28802

August, 1973

AFRPL-TR-73-33

Classified by: AFRPL/MK
Subject to General Declassification
Schedule of Executive Order 11652
Declassified on December 31, 1979

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Proprietary Information; 17 April 1973. Other
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AFRPL (STINFO), Edwards, CA 93523

AIR FORCE ROCKET PROPULSION LABORATORY

DIRECTOR OF SCIENCE AND TECHNOLOGY

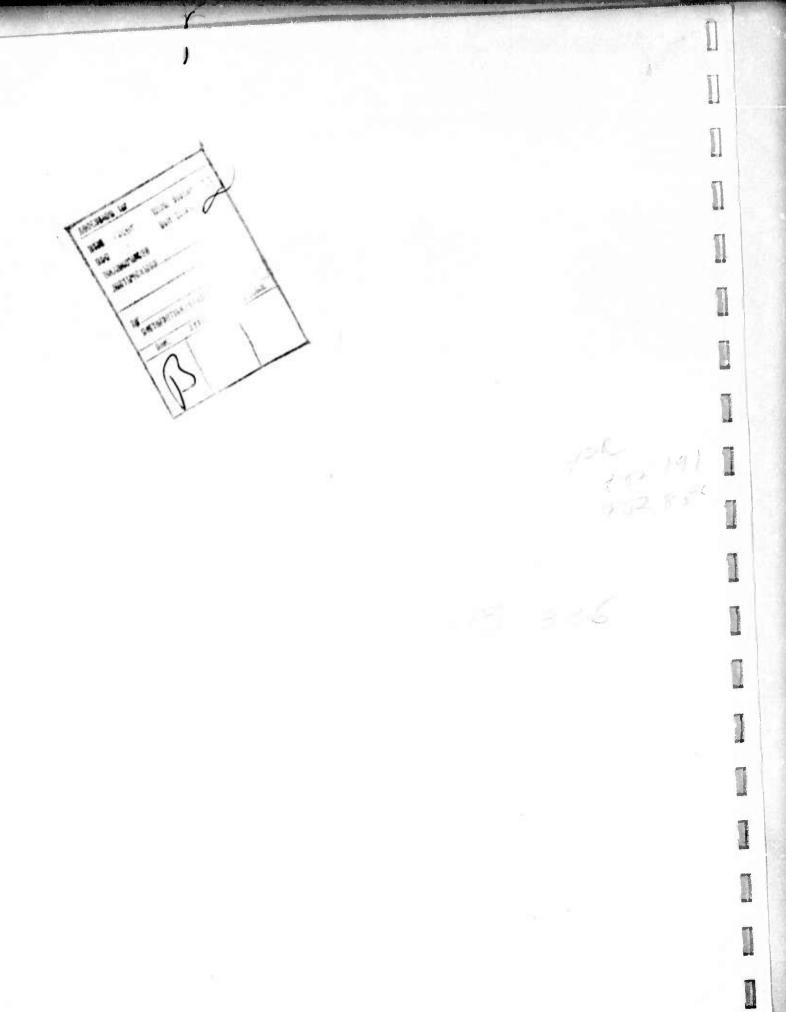AIR FORCE SYSTEMS COMMAND

EDWARDS, CALIFORNIA

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<u>NOTICE</u>

Northrop Carolina, Inc., has been assigned a patent application by the U. S. Patent Office to cover the Gas Generator Method and Apparatus invention disclosed in this publication, and the Commissioner of Patents has issued a secrecy order thereon. This secrecy order requires that those who receive a disclosure of the subject matter be informed of the existence of the secrecy order and of the penalties for the violation thereof.

The recipient of this report is accordingly advised that this publication includes information which is now under a secrecy order. It is requested that he notify all persons who will have access to this material of the secrecy order.

Each secrecy order provides that any person who has received a disclosure of the subject matter covered by the secrecy order is

"in nowise to publish or disclose the invention or any material information with respect thereto, including hitherto unpublished details of the subject matter of said application, in any way to any persons not cognizant of the invention prior to the date of the order, including any employee of the principals, but to keep the same secret except by written permission first obtained of the Commissioner of Patents, under the penalties of 35 U. S. C. (1952) 182, 186"

Although the original secrecy order forbids disclosure of the material to persons not cognizant of the invention prior to the date of the order, a supplemental permit attached to each order does permit such disclosures to:

"(a) Any officer or employee of any department, independent agency or bureau of the Government of the United States.
(b) Any person designated specifically by the head of any department, independent agency or bureau of the Government of the United States, or by his duly authorized subordinate, as a proper individual to receive the disclosure of the above indicated application.

The principals under the secrecy are further authorized to disclose the subject matter of this application to the minimum necessary number of persons of known loyalty and discretion, employed by or working with the principals or their licensees and whose duties involve cooperation in the development, manufacture or use of the subject matter by or for the Government of the United States, provided such persons are advised of the issuance of the secrecy order."

No other disclosures are authorized, without written permission from the Commissioner of Patents. Penalties for violation of a secrecy order, include a fine of up to $10,000 or imprisonment for not more than two years or both.

It must be understood that the requirements of the secrecy order of the Commissioner of Patents are in addition to the usual security regulations which are in force with respect to classified materials in this report. The usual security regulations must still be observed notwithstanding anything set forth in the secrecy order. In the event that this report shall be declassified, the secrecy order remains in full force until it is specifically rescinded.

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NOTICE

This Final Report, submitted in the performance of Contract No. F04611-70-C-0024, contains a description, including details of construction, function, and operation of a gas generating method and apparatus which was first conceived and first actually reduced to practice at Contractor's private expense, prior to the award of the above contract.

The gas generating method and apparatus described is covered in U.S. Patent Application Serial No. 881,667 filed December 3, 1969 entitled "Gas Generating Method and Apparatus" by John N. Godfrey, a continuation-in-part of an earlier filed patent application, Serial No. 797,038, filed February 6, 1969, same title, same inventor, now abandoned.

Notice is hereby given that on February 12, 1970, the U.S. Patent Office imposed a Secrecy Order, in accordance with Title 35 U.S.C. (1952) Sections 181-188, on patent application Serial No. 881,667 which order has not been rescinded at this date. The Secrecy Order is accompanied by a Permit A which prescribes and restricts disclosure of the subject matter to certain persons or agencies of the United States Government.

Notice is also hereby given that the subject matter of patent application Serial No. 881,667 is exclusively licensed to Airtronics, Inc. for manufacture, use, and sale to the United States Government.

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FOREWORD (U)

(U) This Demand Gas Generator Technology Program was performed by Northrop Carolina, Asheville, North Carolina, for the Air Force Rocket Propulsion Laboratory under Contract FO 4611-70-C-0024. The program was monitored by Capt. Robert Quintana and Ralph Felix of the Solid Rocket Division of the Laboratory.

(U) Work under this contract began on 6 May 1970 and was completed on 15 November 1971. This report summarizes all work accomplished during that time period and is submitted in accordance with contract requirements on 22 December 1971.

(U) This report contains classified information extracted from documents listed under the references.

(U) This technical report has been reviewed and approved.

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ABSTRACT (U)

A nineteen-month technology program was performed by Northrop Carolina, Inc. to demonstrate the ability of a demand gas generator concept to vary mass flow at constant pressure and efficiently meet advanced post-boost propulsion system requirements. The program consisted of a parametric study and preliminary design of a demand gas generator for advanced post-boost propulsion applications, the characterization of a standard propellant and catalyst, the development of improved propellants and catalysts, the development of a pyrotechnic/overlay ignition sytem, the development of an electrical catalyst control system, and system demonstration in twelve-inch diameter gas generator motors. Ten, twelve-inch diameter motor tests were conducted which demonstrated a throttling ratio as high as 38 to 1, a 430-second operation, a 28-pulse simulated post-boost propulsion duty cycle, and the capability of operation at three different pressure levels. All basic program objectives were achieved and the feasibility of the demand gas generator concept for post-boost propulsion application was demonstrated.

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SECTION I - INTRODUCTION (U)

(U) Northrop Carolina research and development programs proved the feasibility of augmenting the burning rate of certain solid propellants with a catalyst external to the propellant grain. The burning rate of these propellants at constant pressure was shown to be a function of the proximity of the catalyst to the burning surface of the propellant.

(U) Gas generator mass flow rate can be varied by the above approach at constant pressure over a wide range, i.e. 10 to 1, in a very short response time, i.e. 0.020 second. The solid propellant grain, contained in a combustion chamber, burns continuously at a rate such that the pressure in the chamber remains constant or oscillates around a preset value. The catalyst is directed toward or away from the propellant surface as chamber pressure falls below or exceeds the preset pressure level, depending on an increasing or decreasing system demand for gas. Gas demand varies with valve flow area changes resulting from the actuation of thruster valves.

(U) The response time of the demand gas generator concept is the time required to open or close a valve. The free volume in the gas generator chamber acts as a buffer to pressure changes resulting from variations in gas demand. The variation in chamber pressure with a change in gas demand is thus a function of the chamber free volume and the time required to move the catalyst a distance corresponding to the burning rate extremes, i.e. 0.10 inch.

(U) The objectives of this program were to advance the state-of-the-art of the demand gas generator concept and determine its feasibility for use in post-boost propulsion applications.

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SECTION II - SUMMARY (U)

(U) The Demand Gas Generator Technology Program consisted of three principal tasks. These were 1) a preliminary design study to determine optimum propellant and motor characteristics, 2) the development of a baseline propellant, catalyst, ignition, and control system followed by demonstration in twelve-inch diameter motors, and 3) the development of improved propellant and catalyst systems.

(C) The preliminary design study determined the effect of propellant specific impulse, burning rate, throttling ratio, motor diameter, and chamber pressure on the weight and envelope of an advanced dual chamber post boost propulsion system. For the design requirements used, the optimum propellant and motor characteristics determined were:

Mixture Ratio	4 to 5
Throttling Ratio	15 to 18
Chamber Pressure (psia)	400
Diameter (in.)	16
Burning Rate (ips)	0.092 to 0.116

*(U) The baseline system propellant, R-500, and catalyst, chromic oxide chemically deposited on stainless steel screen, were characterized in three-inch diameter motors in preparation for subsequent twelve-inch diameter motor tests.

(U) An electrical catalyst control system was developed for the twelve-inch diameter motor. This control system can be adapted for use on a flightweight propulsion system. The controller development consisted of analysis of potential control techniques, the selection of the three most promising designs, and fabrication and cold gas testing of the system finally selected (an

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electrical control with high torque, fast response, and reliable operation.).
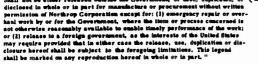
(U) Three ignition methods (electrical, pyrogen, and pyrotechnic) were analyzed. Pyrogen and pyrotechnic igniters were selected for evaluation in three-inch motor tests because of their shorter ignition time, lighter weight, and developed status. The pyrotechnic system was selected for final development due to its higher reliability and shorter ignition time than the pyrogen. The pyrotechnic system consisted of an external igniter with a nitroplastisol propellant overlay on the main grain surface which produced a high heat flux to the grain and catalyst. This pyrotechnic system was tested in the twelve-inch diameter motor and proved satisfactory for the system tests.

(U) Ten twelve-inch diameter baseline system motor tests were conducted using the aforementioned catalyst, R-500 propellant, control system and pyrotechnic igniter. These tests demonstrated:

1. Satisfactory ignition

2. Test durations, in a bistable mode, of up to 420 seconds

3. Mass flow ratios as high as 16 to 1 at any constant chamber pressure between 200 and 600 psia

4. Mass flow ratios as high as 38 to 1 if the chamber pressure was allowed to vary from 200 to 600 psia

5. Catalyst control system response of 20 to 25 milliseconds from signal to catalyst movement.

*(U) Two castable guanidine nitrate propellants were developed in the improved technology portion of the program. One propellant contained a carboxy-terminated polybutadiene binder and the other a fluorocarbon binder. A throttling ratio of 6 to 1 was demonstrated in three-inch diameter motor tests with a polybutadiene propellant and a throttling ratio of 17.4 to 1 was

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demonstrated with the fluorocarbon system. The specific impulse and
mechanical properties of both propellants were superior to those of the base-
line propellant, R-500. Lower propulsion system weights were obtained
in the preliminary design study with use of these improved propellants than
with R-500.

*(U) Alternate chromic oxide catalysts were investigated. These in-
cluded chromic oxide pellets, chromic oxide on a honeycomb structure,
electrophoretic deposited chromic oxide on stainless steel screen, and
plasma-sprayed chromic oxide on steel screen. The electrophoretic and
plasma-sprayed catalysts were more active than the others and comparable
to the baseline catalyst.

(U) All basic program objectives were achieved and the viability of the
solid propellant demand gas generator concept for application in post-boost
propulsion systems was demonstrated.

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SECTION III - PRELIMINARY DESIGN STUDY (U)

1. INTRODUCTION (U)

(U) The objective of the demand gas generator design study was the determination of the effect of several independent variables on the weight and envelope of a dual chamber post-boost propulsion system. The independent variables studied were: 1) propellant specific impulse, 2) chamber pressure, 3) propellant burning rate throttling ratio and 4) gas generator diameter.

(U) A summary of the Preliminary Design Study is contained in this final report. Details of the study were presented in "Demand Gas Generator Design Study Report", NCR-243-71/R1, dated August, 1971, by Northrop Carolina, Inc., Asheville, North Carolina.

2. DESIGN STUDY CRITERIA (U)

(U) The design criteria established by AFRPL is outlined in Table I, and represents a typical mission with attitude control requirements.

(U) For all designs, the number of payloads, the weight of each payload and the delta velocity imparted to each payload was held constant. This provides a comparison of post-boost propulsion systems that will perform the same mission.

3. PARAMETRIC STUDY (U)

a. Propellant Systems (U)

(U) Three propellant systems were studied and the weight optimum conditions occurred at these levels of the independent variables:

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TABLE I - DESIGN STUDY CRITERIA (C)

A. PERFORMANCE

1. Axial

Axial Thrust (maximum)	2000 lb.
Delta Velocity (maximum)	250 fps
Delta Velocity (minimum)	43 fps
Thrust modulation	NR*
Thrust Vectoring (omni-axial)	12° in 1 sec.

2. Attitude Control

Pitch/Yaw Thrust (each of two)**	60 lb_f
Roll Thrust (each of two)	10 lb_f
Total Impulse	30,000 lb_f-sec.
Number of Thrusters, Pitch	4
Number of Thrusters, Yaw	4
Number of Thrusters, Roll	4
Expansion Ratio	60

3. Interstage

Valve	Two-stage/on-off

B. ENVELOPE

Allowable Length	130 in.
Allowable Diameter	22 in.
ACS Diameter	84 in.

C. THRUST MOTOR

Design	Current TCC

* NR = not required.
**Not required during axial thrusting

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DESIGN STUDY CRITERIA (C) - Continued

Mixture Ratio	4-5
Throttling Ratio	15-18
Chamber Pressure, psia	400
Diameter, in.	16
Required Burning Rate, ips	0.092 - 0.116

*(U) The three propellant systems studied were: 1) R-500, a pressed system of only guanidine nitrate, 2) C_7, a castable system using a fluoroacrylate binder and containing guanidine nitrate and ammonium perchlorate, and 3) CTPB, a castable system using a carboxy terminated polybutadiene binder and containing guanidine nitrate and ammonium perchlorate. For this study, a standard prepared catalyst bed of chromic oxide on stainless steel was used.

b.   Throttling Ratio   (U)

(C) Increasing the throttling ratio (ratio of minimum mass flow to maximum mass flow) reduces the propulsion system weight (see Figure 1).   An increase from 5 to 10 decreases the system weight by 3.2 percent. An additional increase in throttling ratio to 15 will result in an additional weight decrease of 1.1 percent. However, the minimum mass flow must meet the requirements of roll thrust which is required continuously. Therefore, throttling ratios higher than 18 for R-500 and 16.5 for C_7 do not decrease the system weight.

(C) At a throttling ratio of 16, the CTPB propellant provides a 44 lbm lighter system than does the C_7 propellant (see Figure 1). However, at the CTPB and C_7 throttling ratios demonstrated (6 and 16, respectively), neither system has a weight advantage. Both systems weigh 1356 lbm.

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GAS GENERATOR THROTTLING RATIO

TOTAL SYSTEM WEIGHT AS A FUNCTION OF THROTTLING RATIO AND PROPELLANT

FIGURE 1

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c. Mixture Ratio and Specific Impulse (U)

(C) For all three propellant systems, the difference in propulsion system weight for the range of oxidizer to fuel mixture ratios from three to five was less than two percent. At a constant mixture ratio of five and a constant throttling ratio of 10, a decrease of up to 0.5 percent in total propulsion system weight can be realized for each unit increase in specific impulse.

(C) The effect of specific impulse at constant mixture ratio can be estimated by comparing the propulsion system weights for the three propellant combinations. This is presented in Figure 2 with a constant 10-to-1 throttling ratio and a 5-to-1 mixture ratio. This shows an approximate decrease of two to 8 pounds in total system weight for each unit increase in specific impulse, when the throttling ratio is constant.

(U) As shown in Figure 2, the higher specific impulse of the CTPB propellant indicates it has a weight advantage; however, this advantage is nearly overcome by the extra propellant needed because of its demonstrated low throttling ratio (6 for the CTPB as compared to 16 for C7).

d. Chamber Pressure (U)

(C) The gas generator chamber pressure for optimum weight on all propellant systems is 400 psia. Chamber pressures as low as 250 psia or as high as 750 psia may be used with a 0.7 percent increase in propulsion system weight. In all runs, the weight optimized, thrust motor chamber pressure was 105 ± 5 psia.

(U) Figure 3 shows a comparison of the total system weight as a function of propellant system and gas generator

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Mixture Ratio   5
Throttling Ratio   10
System Diameter   22 in.
Gas Generator Pressure   600 psia

Thrust Motor Propellant   TP-F1006

Axial Specific Impulse, lb_f-sec/lb_m

Propulsion System Weight, lb_m

(c) Dual Chamber System Weights As A Function Of Specific Impulse (u)

FIGURE 2

M.R. = Mixture Ratio
T.R. = Throttling Ratio

System Diameter   22 in.

Thrust Motor Propellant   TP-F1006

R-500
M.R. = 4
T.R. = 10

T.R. = 16, M.R. = 5   C7

CTPB
M.R. = 2
T.R. = 6

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Gas Generator Chamber Pressure, Hundreds Psia

10   9   8   7   6   5   4   3   2

Total System Weight as a Function of G.G. Pressure and Propellant

FIGURE 3

Total System Weight, LBM

1460   1440   1420   1400   1380   1360   1340

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chamber pressure.

e. <u>Gas Generator Diameter</u> (U)

(C) The results of a series of runs showing the effect of varying the gas generator diameter on the propulsion system weight are shown in Figure 4.   For ease of computations during these runs, the thrust motor diameter was maintained at the present designed diameter of 22 inches.

(C) A weight savings of approximately four pounds per inch (0.3 percent) decrease in gas generator diameter can be achieved. The length increase for each inch decrease in diameter is about three inches.
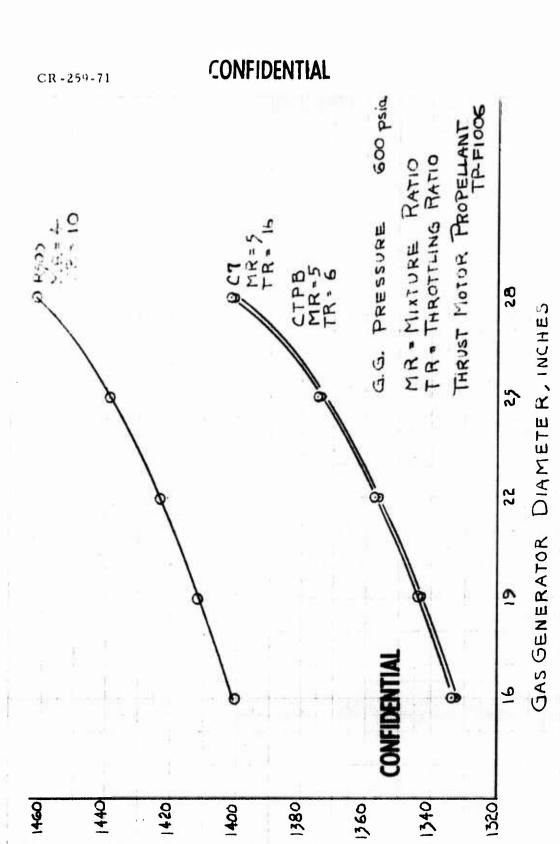
f. <u>Response Time</u>   (U)

(U) The response time for ACS thrust pulses is the time required to open or close the ACS thrusters. This response time for the size thrusters used is in the range of 10-15 msec.

(U) The response time of the catalyst control system determines the amount of chamber pressure undershoot and overshoot in the gas generator. It has been determined from previous studies that the response times of the control system will keep the chamber pressure overshoot to less than five percent of the pressure control level set for the generator.

g. <u>Mission Flexibility</u> (U)

(U) The amount of propellant designed into the gas generator for use by the ACS may be used at any time during coast periods of the mission. This propellant may be utilized at any level between maximum and idle mass flow levels and may be exhausted through any of the ACS thrusters. In these respects, complete

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TOTAL SYSTEM WEIGHT AS A FUNCTION OF G.G. DIAMETER

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ACS mission flexibility exists in the demand gas generator system.

(U) The amount of axial impulse designed into the dual chamber system may be utilized at any time during the mission. Total axial impulse deliveries of less than the design amount may be obtained by not exhausting the generator gas through the thrust motor. This results in unused thrust motor propellant remaining at the end of the mission. Any gas generator propellant not used for axial thrust may be exhausted through the ACS.

<u>h.</u>   <u>Design Comparison</u>   (U)

(U) Table II compares propulsion system designs using each of the three propellant systems with a "best" design using a fictitious propellant having the best properties of each propellant and the desired burning rate. Propulsion systems using either C_7 or CTPB propellant are about 3.4 percent heavier than the best design. However, the system using CTPB propellant is the longest of the two castable systems because of its smaller gas generator diameter.

4.   PRELIMINARY DESIGN   (U)

(U) A demand gas generator dual chamber propulsion system to provide mass flow for both attitude control and delta velocity according to the requirements outlined in Section III-2 is described in Table III.

(U) A single end burning design was selected for the demand gas generator because of its simplicity and ease of design. The C_7 fluoroacrylate propellant was selected for use in the demand gas generator because of its demonstrated throttling ratio even though it needs some burning rate modifications for use in this design.

(U) This preliminary design as presented represents future

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TABLE II -

PROPELLANT CAPABILITIES IN SYSTEM DESIGNS (C)

	Best[1]	Demonstrated[2]			
G.G. Design[4]	SEB	SEB	DEB	DEB	SEB
G.G. Propellant	(1)	CTPB	C7	R-500	R-500
G.G. Pressure, psia	400	400	610	400	1000
G.G. Diameter, in.	22	16	22	22	22
Burning Rate, ips	.092	.265	.048	.053	.097
Throttling Ratio	16	6	16	10	10
Mixture Ratio	5	3	5	5	6
Specific Impulse, lb_f-sec/lb_m [3]					
ACS	207.4	207.4	202.4	199.0	199.0
Axial	252.7	259.4	243.5	234.5	232.5
System Weight, lb_m	1311	1355	1383	1444	1442
System Length, in.	97.4	119.1	103.9	120.5	115.6

[1] Using the best properties of all three propellants

[2] Using the demonstrated properties of each propellant

[3] Theoretical delivered at motor conditions

[4] SEB = Single End-Burning Grain
DEB = Dual End-Burning Grain

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TABLE III - PRELIMINARY DESIGN SUMMARY
DEMAND GAS GENERATOR DUAL CHAMBER (C)

I.   PERFORMANCE

     a.   Total System

	Time (sec)	Thrust (lb_f)	Impulse (lb_f-sec)
Axial	108.8	2000	217,514
Pitch[1]	91.7	120	11,000
Yaw[1]	91.7	120	11,000
Roll[2]	400.0	20	8,000

     b.   Gas Generator

Chamber Pressure (psia)		400
Mass Flow (lb_m/sec)		
Axial + Roll	1.468	1.468
Pitch + Yaw + Roll		1.285
Roll[3]		0.099
Duration		
Axial + Roll		108.8
Pitch + Yaw + Roll		91.7
Roll		400.0
Specific Impulse (lb_f-sec/lb_m)[4]		202.4
Catalyzed Burn Rate (in./sec)		0.093
Throttling Ratio		16

     c.   Thrust Motor

Chamber Pressure (psia)	105

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[1] Pitch and yaw thrust simultaneously

[2] Roll thrust for duration of test

[3] Roll mass flow = 0.99 lb_m/sec; idle mass flow = 0.102 lb_m/sec

[4] Vacuum; delivered; 60:1 expansion; 15 deg half angle

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TABLE III - PRELIMINARY DESIGN SUMMARY
DEMAND GAS GENERATOR DUAL CHAMBER (C)

(Continued)

c.   Thrust Motor (continued)

Mass Flow (lb_m/sec)	
From Gas Generator	1. 369
From Thrust Motor	6. 845
Total Axial	8. 214
Duration (sec)	108. 8
Specific Impulse (lb_f-sec/lb_m)[5]	243. 5
Mixture Ratio	5. 0
Burn Rate (in. /sec)	0. 065

II.   DESIGN

a.   Total System Design   Demand Gas Generator
                                        Dual Chamber

b.   Demand Gas Generator

Grain Design	Single end burning
Propellant Diameter (in.)	20. 36
Propellant Web (in.)	16. 94
Case Max. O. D. (in.)	22. 00
Case Thickness (in.)	0. 031
Case Yield Strength (psi)	160, 000
Insulation Thickness (in.)	0. 55
G. G. Length (in.)	27. 20

c.   Interstage

Flow Area (sq. in.)	0. 419
Valve Type	Two stage, on-off
Length (in.)	9. 58

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[5] Vacuum; delivered; 30: 1 expansion; 15 deg half angle

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TABLE III - PRELIMINARY DESIGN SUMMARY
DEMAND GAS GENERATOR DUAL CHAMBER (C)

(Continued)

d.   Thrust Motor

Grain Design	Internal burning - finned CP
Propellant O. D. (in.)	21.95
Propellant Web (in.)	7.08
Case Max. O. D. (in.)	22.00
Case Thickness (in.)	0.025
Case Yield Strength (psi)	240,000
Insulation Thickness (in.)	0.69
T. M. Length (in.)	41.30

e.   Axial Nozzle   Contoured

Throat Area (sq. in.)	10.36
Throat Diameter (in.)	3.63
Expansion Ratio	30
Half Angle (equivalent), deg	15
Vector (deg)	12
Nozzle Length (in.)	22.34

f.   Attitude Control

	Pitch	Yaw	Roll
No. of Thrusters	4	4	4
Thruster Type	two stage, on-off	two stage, on-off	single stage, on-off
Flow Area (sq. in.) (each)	0.090	0.090	0.015
Expansion Ratio	60	60	60
Valve Length (in.)	3.37	3.37	1.95
Exit Length (in.)	2.79	2.79	1.14
Duct Length (in.)	36.5	36.5	---
Duct I. D. (in.)	0.58	0.54	---
Duct O. D. (in.)	1.86	1.82	---
Duct Weight (lb_m/ft)	0.68	0.65	---

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TABLE III - PRELIMINARY DESIGN SUMMARY

DEMAND GAS GENERATOR DUAL CHAMBER (C)

(Continued)

III.   WEIGHT (lb_m)

		Pitch	Yaw	Roll
a.	**Propellant**			1042. 12
	Gas Generator		297. 72	
	Axial	148. 90		
	ACS	148. 21		
	Idle [6]	0. 61		
	Thrust Motor		744. 40	
b.	**Inert**			342. 64
	Gas Generator			78. 88
	Case		22. 11	
	Cylindrical Section	5. 60		
	Domes (2)	4. 54		
	Skirts (2)	3. 93		
	Flange	7. 91		
	Bosses (2)	0. 13		
	Insulation		30. 54	
	Activator Assembly		24. 23	
	Igniter		2. 00	
	Interstage			19. 30
	Valve		13. 50	
	Plenum		1. 21	
	Ducting		1. 69	
	Thermal Barrier		1. 12	
	Attachment		1. 78	
	Attitude Control System			30. 93
	Thrusters		9. 30	
	Ducting		16. 20	
	Exit Cones		4. 00	
	Flanges		0. 93	

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[6] Above needed for roll during roll only phases

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TABLE III - PRELIMINARY DESIGN SUMMARY
DEMAND GAS GENERATOR DUAL CHAMBER (C)

(Continued)

b. Inert (Continued)

	Pitch	Yaw	Roll
Thrust Motor			85.52
Case		34.34	
Cylindrical section	12.34		
Domes (2)	8.49		
Bosses (2)	9.27		
Skirt	4.24		
Insulation		37.70	
Diffuser		13.48	
Control and Cabling			43.47
Contingency			14.71

c. Total System   1389.76

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technology in the areas of the catalyst control system, the catalyst drive system and the demand gas generator propellant.

(U) The thrust motor and nozzle designs are present state-of-the-art as described by Thiokol Chemical Corporation.[1] Duct and valve designs also represent present technology.

(U) The preliminary design as presented herein represents the optimum parameters as defined by the parametric study. However, several changes have been made to the computerized designs to reflect the latest design practices and technology. Major areas of change were:

1) The control system power supply was changed from an electric motor to a warm gas turboactuator and located outside of the chamber rather than internally. This increased the system length by 8.5 inches.

2. Weight changes to reflect the exact preliminary design as presented.

5. SYSTEM COMPARISON (U)

(U) The weight of four different post-boost propulsion designs were compared and are presented in Tables IV, and V. The design weights of 1) a conventional gas generator only, 2) a demand gas generator only, 3) a conventional gas generator dual chamber, and 4) a demand gas generator dual chamber which meet the basic mission requirements were compared. The demand gas generator dual chamber system was 24 percent lighter than the conventional gas generator dual chamber system and was less than a third of the weight of the conventional gas generator only system.

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[1]"Final Report - Dual Chamber Solid Post-Boost Propulsion Study", Dec. 1970, Thiokol Chemical Corporation, Wasatch Division, Technical Report SAMSO TR-71-67.

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TABLE IV - DESIGN SUMMARY(C)

	Single Chamber		Dual Chamber	
	Conventional G.G.	DGG	Conventional G.G.	DGG
Gas Generator				
Propellant Type	Nitro-plastisol	Fluoro-acrylate	Nitro-plastisol	Fluoro-acrylate
Specific Impulse (lb_f-sec/lb_m) Axial[1]	204.4	198.4	---	---
ACS[2]	209.5	202.4	209.5	202.4
Chamber Pressure (psia)	400	400	400	400
Total Duration (sec)	400	400	400	400
Burn Rate Required (ips)	0.548	0.643	0.090	0.093
Throttling Ratio	1	16	1	16
Design[3]	SEB	SEB	SEB	SEB

Thrust Motor		
Propellant Type	TP-F1006	
Specific Impulse[1] (lb_f-sec/lb_m)	260.0	243.5
Chamber Pressure (psia)	120.0	105.0
Duration (sec)	113	109
Mixture Ratio	4	5
Design	Finned CP	

[1] Vacuum; delivered; 30:1 expansion; 15° half angle

[2] Vacuum; delivered; 60:1 expansion; 15° half angle

[3] SEB = single end-burning grain design

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TABLE V - WEIGHT COMPARISON SUMMARY (C)

	Single Chamber[1]		Dual Chamber[2]	
	Conventional G.G.	DGG	Conventional G.G.	DGG
Propellant				
Gas Generator				
Axial	1574	1265	174	149
ACS	143	148	143	148
Idle	2235	112	337	1
Total	3952	1525	654	298
Thrust Motor	---	---	696	744
Inert				
Gas Generator	305	154	82	67
Interstage .	---	---	23	19
Thrust Motor	---	---	66	64
Nozzle	45	45	65	69
ACS	31[3]	31	31[3]	31
Control and Cable	48	48	48	48
Contingency	16	16	16	16
Total	445	294	331	314
Total System	4397	1819	1681	1356

[1] No thrust vector control; axial exhaust through an on-off valve with 30:1 expansion cone.

[2] Thrust vector control = 12°

[3] No provisions for excessive dumping

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SECTION IV -

DEVELOPMENT OF THE BASELINE SYSTEM (R-500) (U)

1. INTRODUCTION (U)

(U) The feasibility of augmenting the burning rate of certain solid propellants with a catalyst external to the propellant grain was proven by Northrop Carolina research and development programs.

(U) To advance the state-of-the-art of the demand gas generator concept and determine its feasibility for use in post-boost propulsion applications, it was necessary to explore the potentials of a baseline system. Simultaneous to the development of the baseline system, investigations were initiated on improvements to propellants, catalysts, catalyst bed supports, and liner materials.

(U) The primary objectives of the baseline system development were to measure equilibrium and transient performance of the propellant, to demonstrate a significant throttling ratio at constant pressure, and determine response times and durability of the twelve-inch diameter gas generator.

2. APPROACH (U)

(U) In order to identify and eliminate anomalies in test data due to processing and fabrication variations, processing and fabrication specifications were established and travelers and logs were maintained throughout the program.

(U) Particular emphasis was placed on the characterization of the baseline, R-500 propellant and the fabrication and assembly techniques used on the standard catalyst bed.

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(U) Each phase of the baseline system development program started with an intensive literature survey. Sub-tasks under the baseline system development effort such as the ignition and control system development included analyses and comparisons of two or more methods to complete their specific objectives. In several instances, consultants and vendors were contacted.

(U) Three-inch diameter test hardware was used to gather data when scaling effects were minimal or accountable to conserve test costs.

(U) Individual components were tested when possible to prevent a single component's malfunction from destroying other parts of a subsystem. The catalyst bed controller subsystem was tested with cold gas before it was subjected to hot gas testing.

(U) The development of each subtask was arranged to integrate with the complete baseline system. Following are specific approaches and accomplishments for the subtasks.

3. DESIGN

(U) A 12-inch diameter test motor capable of containing a 50 lb_m propellant grain was designed and fabricated. This test vehicle was equipped with up to three on-off valves to vary the flow area and, hence, the thrust. A bistable control system was used during these tests to maintain "constant" chamber pressure by controlling the catalyst screen standoff distance.

(U) The catalyst beds were fabricated from three layers of prepared catalyst screens fastened to Waspalloy support structures.

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Catalyst screens were prepared by impregnating flame-sprayed stainless steel screens with chromic oxide by dipping them in ammonium dichromate prior to firing them.

(U) The 12-inch diameter demand gas generator design was similar to the three-inch diameter test device in that the end burning propellant grain was contained in a cylindrical pressure chamber and the catalyst bed was attached to a vertical rack above the propellant surface. Figure 5 is a schematic of the 12-inch diameter, demand gas generator test device, and Figure 6 is a schematic of the three-inch diameter demand gas generator test device.

(U) The propellant was cartridge loaded into the device. Figure 5 shows one valve, but by extending the arrangement with a manifold, configurations with as many as three valves were tested.

(U) The size and weight of the "cover" necessitated a pneumatic lifting mechanism. This was designed into the test stand. Six "tie rods" between the base and the cover were used to maintain pressure seals.

(U) "Desired catalyst position" was obtained by monitoring and comparing the chamber pressure with two preset pressure levels. If the chamber pressure were above the maximum preset level, the catalyst was retracted away from the propellant. If the chamber pressure were below the minimum preset level, the catalyst was moved until it was in intimate contact with the propellant.

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SCHEMATIC OF 12-INCH GAS GENERATOR

ACS Simulator

Control Mechanism Not Shown

Control Rod

Constant Flow Nozzle

Pressure Equalizing Duct

Pneumatic Valve Actuator with DC Solenoid Valve

Valve Position Indicator

On-Off Valve

Catalyst Support

Catalyst

Ignition Layer

Pressure Chamber

Grain Cartridge

Support

Pressure Terminal with Ignition Lead

11.5 Dia

10.0

*Proprietary Data

Figure 5
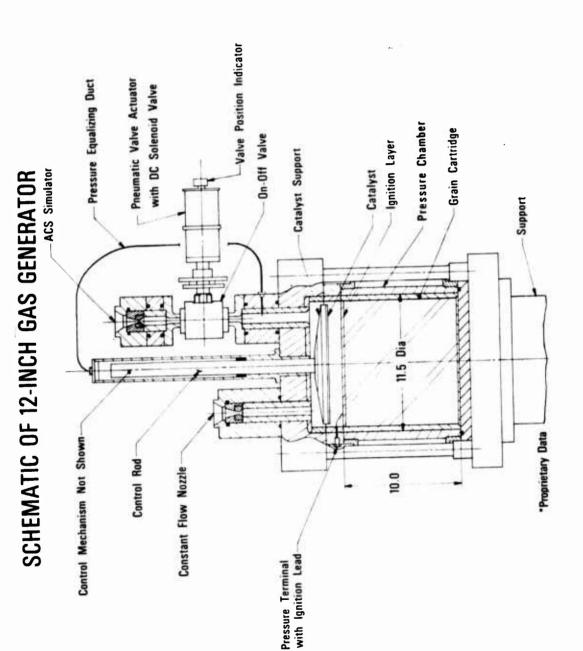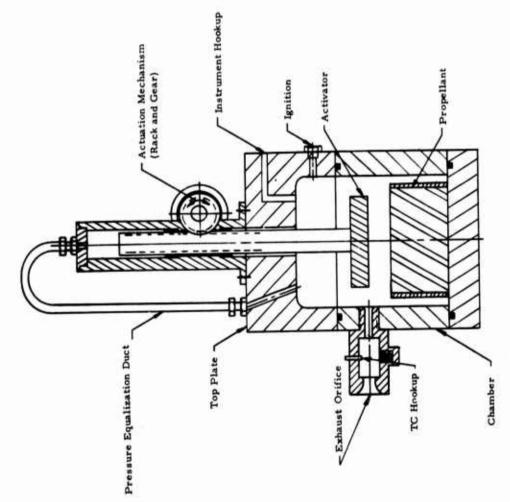
Schematic of 3-Inch Test Weight Gas Generator

Actuation Mechanism (Rack and Gear)

Instrument Hookup

Ignition

Activator

Propellant

Pressure Equalization Duct

Top Plate

Exhaust Orifice

TC Hookup

Chamber

PROPRIETARY DATA*

Figure 6

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4. R-500 PROPELLANT CHARACTERIZATION (U)

    a. Introduction (U)

        (U) A study was conducted to determine the ballistic, physical, and thermal properties of R-500 propellant in order that design limitation could be established for future propulsion systems containing this baseline propellant.

        (U) R-500 propellant was substituted for R-501 for this study based on previous work[2] which showed that the binder in R-501 did not improve processability or mechanical properties. Compressive strength tests were substituted for tensile tests to characterize the effect of temperature, strain rate, and aging on mechanical properties. This change was made to detect small variations in propellant properties which might go undetected due to the scatter in tensile measurements.

        (U) The ballistic properties of R-500 propellant were characterized between the pressures of 250 and 800 psia in vertical tests and data were generated for use in designing future propulsion systems between -65 and +160°F. Two horizontal tests were also performed and the attitude did not effect ballistic performance. The physical properties of R-500 propellant were characterized between -65 and +165°F.

    b. Parameters Investigated (U)

        (1) General (U)

            (U) In order to eliminate variables other than those to be evaluated, components of the three-inch

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[2] NCR-191-70, Effect of Pressing Procedure, Oxidizer Purity, Binder Content, and Mix Aging on the Physical Properties of R-501 Propellant, 25 August 1970.

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diameter generator test bed, used for the characterization, were standardized or controlled.

(a) Guanidine Nitrate *(U)

(C) The guanidine nitrate used for pressing the three-inch propellant charges was from one lot of material, and was categorized into three purity grades described in Table VI Table VII describes the process for obtaining each grade. Grade II was the type used in the standard or baseline, R-500 propellant and the other two grades were used in R-500 propellant for burn rate reproducibility tests. All of the propellant grains of each grade for characterization tests were fabricated from one batch of the respective grade of material.

(b) R-500 Propellant Processing (U)

(U) Process procedure NPS-1143, "Process Specification for Pressing R-500 Propellant Charges," was prepared and released. A Propellant Press Sheet was used as the process traveler and was filled out during manufacturing by the cognizant technician.

(c) Catalyst (U)

(U) A process procedure for standard catalyst preparation, NPS-1145, "Process Specification for Catalyst Bed Preparation," was prepared and released. A manufacturing traveler containing pertinent data was filled out during the fabrication. After manufacture, each catalyst bed was placed in a protective and identification envelope.

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Table VI - Properties of Guanidine Nitrate *(U)

Property	As Received	Grade I	Grade II	Grade III
Composition (wt. %)				
Oxidizer				
Wet	91.58	92.33	98.68	99.61
DSC	----	----	96.01	98.96
Ammonium Nitrate	6.09	4.04	0.87	0.18
Melamine	1.48	1.48	0.62	0.13
Volatiles	0.45	0.15	0.11	0.05
pH, 10% Aqueous Solution	6.79	4.49	4.35	4.12
Melting Point, (^{o}C)	189-205	199-201	209-212	212-214

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Table VII - Process For Preparation Of Oxidizer   (U)

Grade		Procedure
I	a.	As received material is dried for 24 hours at 105 - 110°C.
	b.	The dried material is micropulverized.
II	a.	As received material is washed with 1.5 parts water to 1.0 part oxidizer for 20 minutes at 10 - 15°C water temperature.
	b.	Filtered and slurry washed with 0.2 parts acetone.
	c.	Dried at 105 - 110°C for 24 hours.
	d.	The dried material is micropulverized.
III	a.	The as received material is dissolved in 3.0 parts water to 1.0 part oxidizer at 70 - 80°C and filtered.
	b.	The solution cooled to 25°C at a rate of 12°C per hour to obtain 300 micron oxidizer.
	c.	Crystals filtered and dried at 105 - 110°C.

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(U) The relative light permeability of each bed was checked and recorded, using a fixed light source and a photocell.

(U) The relative catalytic activity of each bed was checked and recorded. Activity comparison entailed weighing a three-inch diameter grain, heating the catalyst bed to $1500^{\circ}F$, placing the bed on the propellant and weighing the R-500 grain again to determine the propellant consumed.

(d) Ignition (U)

*(U) The three-inch diameter characterization motor ignition technique was standardized. It consisted of lowering a hot catalyst bed down on a pressed ammonium nitrate-guanidine nitrate wafer which was on the R-500 grain surface. The pressed wafer process procedure conformed to NPS-1149.

(2) Sensitivity of Burning Rate to Temperature (U)

(U) Thirty, three-inch diameter propellant R-500 grains were pressed from one batch of Grade II guanidine nitrate in accordance with the established procedure, NPS-1143. These grains were dimensionally and radiographically inspected prior to being placed in temperature conditioning at $-65^{\circ}F$, $70^{\circ}F$, and $165^{\circ}F$ (ten at each temperature). They were then static tested in Northrop Carolina, Inc.'s three-inch diameter test motor in accordance with Test Procedure TEST-143. The catalyst and igniter were baseline as described above. Five propellant grains were tested at each of the three temperatures and at each of

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two K_n values. The catalyst was held in constant contact with the propellant surface during the entire test of each grain.

(U) The R-500 propellant grains, catalyst beds and overlay grains, together with the pertinent data for each, and the combination of these items used for each test are given in NCR-219-71, "Characterization of Ballistic, Physical, and Thermal Properties of R-500 Propellant." The reduced test data are presented in Table VIII.

(U) The burn rate-pressure data for motors tested at $70^{\circ}F$ were evaluated and a least squares fit burn rate curve was established. The $70^{\circ}F$ vertical tests of Grade II material from the burn rate reproducibility portion of the characterization were also included as additional data from the same batch of grains. This additional data increased the confidence in the burn rate relationship. The resultant burn rate-pressure relationship is shown in Figure 7. The K_n-pressure relationship is also shown at $70^{\circ}F$ for these same data. The K_n curve was established by an arithmetic average of the measured pressures for each K_n.

(U) The data for the motors tested at $-65^{\circ}F$ and $+160^{\circ}F$ were treated in a similar manner and the burn rate and K_n as functions of pressure are shown in Figures 8 and 9 respectively.

(U) From the burn rate and K_n data presented in the figures, the following relationships were determined:

● Burn rate sensitivity to temperature at constant pressure (σ p)

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TABLE VIII - REDUCED DATA FROM TEMPERATURE SENSITIVITY TESTS (U)

Test No.	Date Tested	Cond. Temp.	K_n	K_n Equil Press(psia)	Burn Rate (in/sec)	Burn Rate Pc (psia)	C* (ft/sec)	Flame Temp.(°F)
24	10-19-70	+70°F	1784	779	0.0837	782	2862	1329
25	10-19-70	"	"	748	0.0982**	740	2578	1123
26	10-19-70	"	"	676	0.0863	688	2743	1269
27	10-19-70	"	"	643	0.0816	680	2852	1197
28	10-19-70	"	"	618	0.0839	658	2677	1171
79	11-6-70	"	1102	291	0.0524	298	3090	801
80	11-9-70	"	"	280	0.0451	294	3547	775
169	1-7-71	"	1092	263	0.0438	254	2847	614
170	1-7-71	"	"	325	0.0649	330	2898	738
171	1-7-71	"	"	283	0.0538	283	2952	934
41	10-20-70	+160°F	1784	657	0.0867	657	2891	1348
77	11-6-70	"	1866	722	0.0713	738	3419	1076
43	10-20-70	"	1784	748	0.0991	763	2736	1374
44	10-20-70	"	1784	546*	0.0792	653	2808	1059
45	10-20-70	"	1784	824*	0.1042	829	3012	1084
72	11-6-70	"	1186	416*	0.0710	416	3106	1088
73	11-6-70	"	1186	331	0.0581	324	3092	1192
74	11-6-70	"	1186	369*	0.0720	371	3151	1153
75	11-6-70	"	1186	387*	0.0720	398	3198	1050
76	11-6-70	"	1186	373*	0.0636	387	3188	1148
52	10-26-70	-65°F	1802	422	0.0498	424	2912	570
53	10-26-70	"	1802	386	0.0443	407	3024	708
55	10-26-70	"	1802	414	0.0540	453	2999	710
56	10-26-70	"	1802	443	0.0496	469	3015	746
78	11-6-70	"	1866	391	0.0463	418	3148	735
67	11-6-70	"	1186	199	0.0304	165	2886	485
68	11-6-70	"	1186	197	0.0428	225	3041	838
69	11-6-70	"	1186	153	0.0320	156	2640	892
70	11-6-70	"	1186	228	0.0397	236	2949	1160
71	11-6-70	"	1186	205	0.0370	201	3021	930

*Did not establish an equilibrium pressure and not used to determine K_n-pressure curve

**Not used for burn rate-pressure relationship
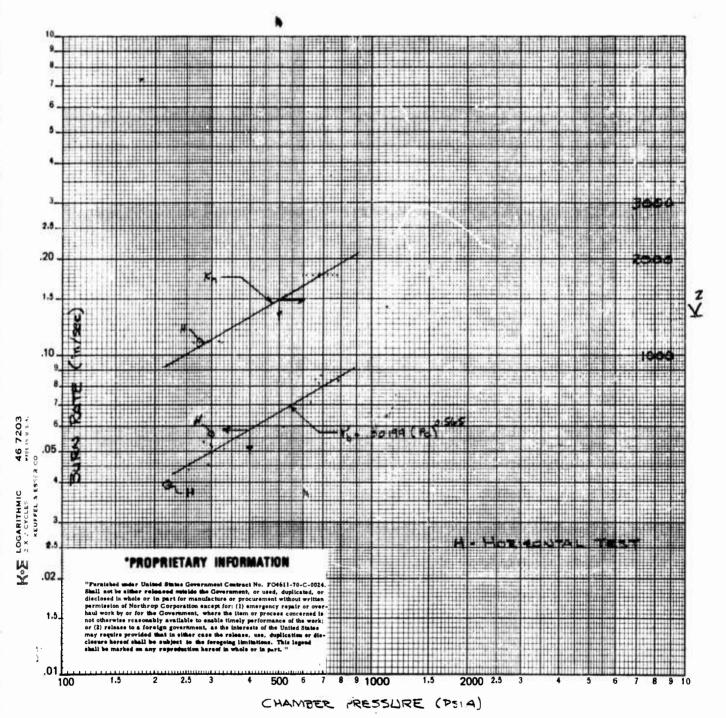
FIGURE 7 - Burn Rate and K_n as Functions of Pressure
R-500 Propellant, 70°F
(Grade II Guanidine Nitrate) (U)*

BURN RATE (r_b /SEC)

K&E LOGARITHMIC 46 7203
KEUFFEL & ESSER CO.

$r_b = .0036 p_c^{.425}$

$\pi_p = 0.13 \%/°F @ 300 psi$
$\pi_p = 0.20\%/°F @ 600 psi$

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CHAMBER PRESSURE (PSIA)

FIGURE 8 - Burn Rate and K_n as Functions of Pressure
R-500 Propellant, -65°F
(Grade II Guanidine Nitrate) (U)*

FIGURE 9 - Burn Rate and K_n as Functions of Pressure
R-500 Propellant, +160°F
(Grade II Guanidine Nitrate) (U)*

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At 300 psi

$\sigma_p = 0.18\%/^oF$ between +70 and +160°F

$\sigma_p = 0.13\%/^oF$ between +70 and -65°F

At 600 psi

$\sigma_p = 0.15\%/^oF$ between +70 and +160°F

$\sigma_p = 0.20\%/^oF$ between +70 and -65°F

- Pressure sensitivity to temperature at a constant K_n (π_k)

At $K_n = 1100$

$\pi_k = 0.023\%/^oF$ between +70 and +160°F

$\pi_k = 0.39\%/^oF$ between +70 and -65°F

At $K_n = 1800$

$\pi_k = 0.047\%/^oF$ between +70 and +160°F

$\pi_k = 0.40\%/^oF$ between +70 and -65°F

- Burn rate sensitivity to temperature at a constant K_n

At $K_n = 1100$

Burn rate temperature sensitivity = 0.20%/^oF 70 to 160°F

Burn rate temperature sensitivity = 0.52%/^oF 70 to -65°F

At $K_n = 1800$

Burn rate temperature sensitivity = 0.20%/^oF 70 to 0°F

Burn rate temperature sensitivity = 0.20%/^oF 70 to -65°F

(U) The σ_p and π_k are common propellant temperature sensitivity factors but the burn rate sensitivity at a constant K_n is not. This factor was arrived at by the

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summation of the $\tilde{\Pi}_k$ factor at the particular constant K_n and the $\tilde{\sigma}_p$ factor at the corresponding constant pressure.

(3) Burn Rate Reproducibility (U)

(U) Burn rate reproducibility tests were performed to compare the ballistic performance of the three different grades of guanidine nitrate. The Grade II material was used in the baseline R-500 propellant. Twenty-one, three-inch diameter motor tests were performed; seven with each grade of material and the propellant grains were conditioned to $70^{\circ}F$. Five of the tests of each material were conducted with the three-inch diameter test motor in the customary vertical attitude and two tests of each were conducted in the horizontal attitude. The propellant grains, catalyst beds, and pressed ignition wafers used in this series of tests, together with the pertinent data for each and the combination of the items used for a particular test is given in NCR-219-71, Characterization of Ballistic, Physical, and Thermal Properties of R-500 Propellant. The reduced test data are presented in Table IX. The burn rate curve for the Grade II material is shown in Figure 7, with the $70^{\circ}F$ temperature sensitivity data. The burn rate and K_n curves for the Grade I and Grade III materials are shown in Figures 10 and 11, respectively. The horizontal test results of each material are specifically identified with an "H." These data were not used to establish the burn rate-pressure and K_n-pressure relationships. The burn rate curves were established by a computer calculated best fit line. The K_n curves were

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TABLE IX - REDUCED DATA FROM BURN RATE REPRODUCIBILITY TESTS (U)

Test No.	Date Tested	Cond. Temp.	K_n	K_n Equil Press (psia)	Burn Rate (in./sec)	Burn Rate (psia)	C* (ft/sec)	Flame Temp. (°F)
15	10-19-70	70°F	1784	660	0.0813	698	2824	1530
16	10-19-70	"	1784	580	0.0703	578	2803	1308
17	10-19-70	"	1784	764*	0.0900	802	2860	1601
29	10-20-70	"	3366	--	0.113	1554	2688	1051
84	11-9-70	"	1102	375	0.0587	381	3497	1048
122(H)	11-23-70	"	1080	320	0.0668	320	2624	465
123(H)	11-23-70	"	1080	385	0.0732	405	2904	620
18	10-19-70	"	1784	726	0.0833	744	2706	1316
19	10-19-70	"	1784	598	0.0712	639	2700	1280
20	10-19-70	"	1784	494	0.0598	515	2786	1214
85	11-9-70	"	1102	280	0.0520	301	3635	1062
86	11-9-70	"	1102	319	0.0511	330	3611	956
124(H)	11-23-70	"	1080	218*	0.0391	218	3061	553
125(H)	11-23-70	"	1080	275	0.0564	299	3475	600
21	10-19-70	"	1784	664	0.0807	658	2631	1146
22	10-19-70	"	1784	725	0.0862	746	3013	1295
23	10-19-70	"	1784	778	0.0907	776	3202	1305
87	11-9-70	"	1102	270	0.0460	275	3478	996
88	11-9-70	"	1102	357	0.0592	369	3623	1060
126(H)	11-23-70	"	1080	213	0.0437	220	2976	581
127(H)	11-23-70	"	1080	287	0.0613	298	2848	553

(H) Horizontal test

* Did not establish an equilibrium not used to establish K_n-pressure curve
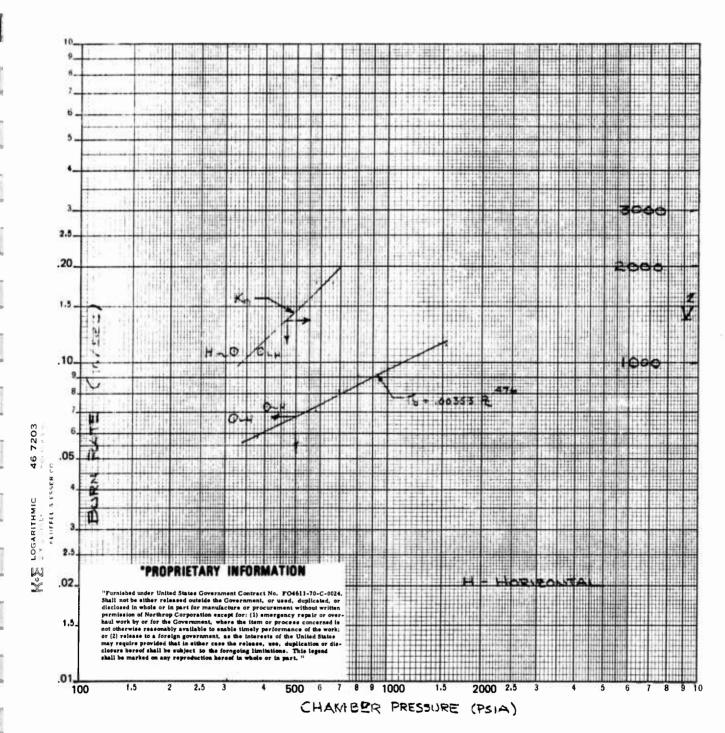
FIGURE 10 - Burn Rate and $\dot{K}_n$ as Functions of Pressure
Modified R-500 Propellant, +70°F
(Grade I Guanidine Nitrate) (U)*

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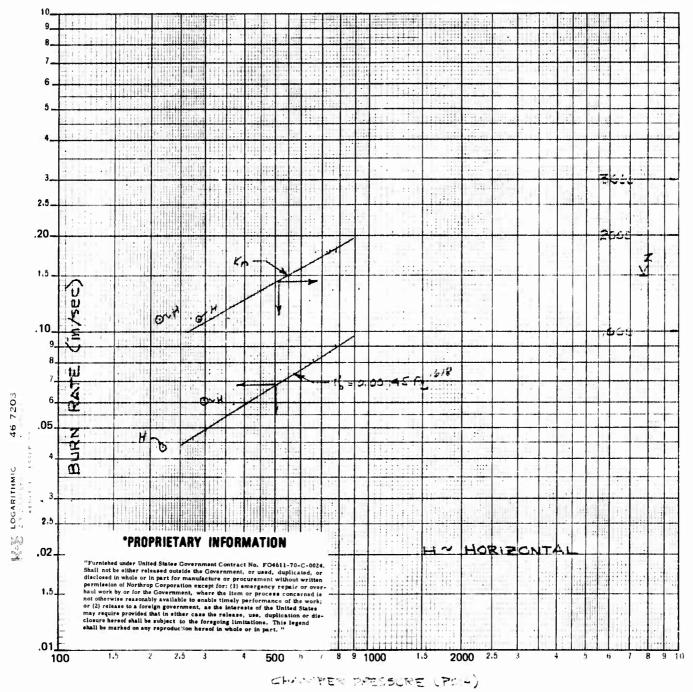
FIGURE 11 - Burn Rate and K_n as Functions of Pressure
Modified R-500 Propellant, +70°F
(Grade III Guanidine Nitrate) (U)*

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established by the arithmetic average of the pressures at the particular K_n values.

(U) The changing of the attitude of the three-inch diameter motor from the customary vertical to horizontal did not appear to effect the motor performance delivered by the Grade II material. The burn rate data appear to be in the range of the data measured in the vertical tests. The Grade III burn rates, however, are varied; one data point appears to be near the vertical motor data (220 psia data) and the other point (298 psia data) noticeably higher than the vertical motor data. The Grade I material burn rates are both higher, for the particular pressures, than the vertical motor test data. A conclusion was not made concerning the comparison of vertical and horizontal tests due to the limited number of horizontal tests.

(U) The vertical motor test burn rate data for the Grade I and III materials do not appear to differ significantly from the Grade II characterization data. There was, however, one noticeable difference in the material grades. The propellant grain densities show that Grade II propellant has a higher pressed density (0.0513 lb/in.^{3}) than either the Grade I (0.0492 lb/in.^{3}) or the Grade III (0.0493 lb/in.^{3}).

(U) Attempts were made to measure the non-catalyzed burn rate, but were not successful. Insulated specimens were placed in various locations in the motor chamber in an attempt to gather meaningful data and it was concluded that it was not feasible to measure noncatalyzed burn rates in the three inch diameter motor. An analytical study

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was performed to determine the non-catalyzed or minimum regression of the propellant surface. This analysis is shown in Appendix of Reference (3).

(4)   Constant Strain-Rate Compressive Properties (U)

(U) Specimens for the constant strain-rate compressive properties were 0.6-inch diameter by 2.0-inch long dowels machined from pressed R-500 grains. The specimens were conditioned at -65^OF, $+70^O$F, and $+165^O$F and evaluated at crosshead speeds of 0.02, 0.2, and 1.0 inch per minute using an Instron Tester equipped with a Messimers temperature conditioning cabinet. Five specimens were tested at each temperature and crosshead speed for a total of 45 tests.

(U) Similar specimens were also prepared from propellant grains pressed at 6000 and 7000 psi to determine the effect of press pressures other than 8000 psi on compressive properties. Five specimens were tested at -65^OF, $+70^O$F, and $+165^O$F at a crosshead speed of 0.2 inch per minute for a total of 30 additional tests.

(U) The measured mechanical properties of R-500 propellant in compression are given in Tables XIII through XVIII of Reference (3). A typical stress-strain curve is shown in Figure 12.   The maximum stress at failure was obtained from the tangent point at the maximum of the curve. At this point, the samples showed visible evidence of failure. Differentiation between maximum and ultimate stress can be made for the propellant in compression. Strain at failure was calculated from the chart distance traveled to the point of failure. The initial modulus was

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Figure 12 Typical Compressive Stress-Strain Curve (U)

determined from the intercept of a line drawn tangent to the initial slope of the curve and a distance representing a known deflection in the sample.

(U) Maximum stress, strain at maximum stress, and initial modulus are plotted as a function of temperature in Figures 13, 14, and 15, respectively. The compressive properties are essentially identical for grains pressed at each of the three pressures, i.e., 6000, 7000, and 8000 psi.

(U) The constant strain-rate compressive properties were further characterized by time-temperature super-position. The experimental data are plotted as a function of reduced time to failure at $70^\circ F$ in Figure 16. The shift factor a_T was determined using the Williams, Landel, and Ferry (WLF) equation. This shift factor is plotted in Figure 17 as a function of temperature.

(U) The poor alignment of the data is likely due to the WLF shift factor not being applicable to this propellant. R-500 propellant may be analogous to a conventional viscoelastic propellant below its glass transition temperature. The temperature dependence of a_T below the glass transition temperature of viscoelastic polymers has been found to follow an equation of the simple Arrhenius form.

$$\log \ a_T = \ (\Delta Ha/R)(1/T - 1/To),$$
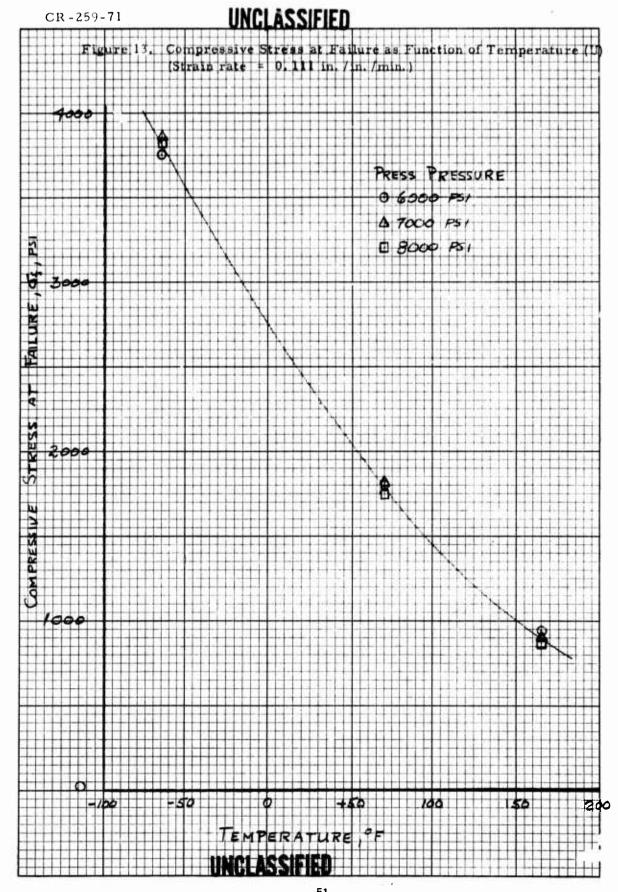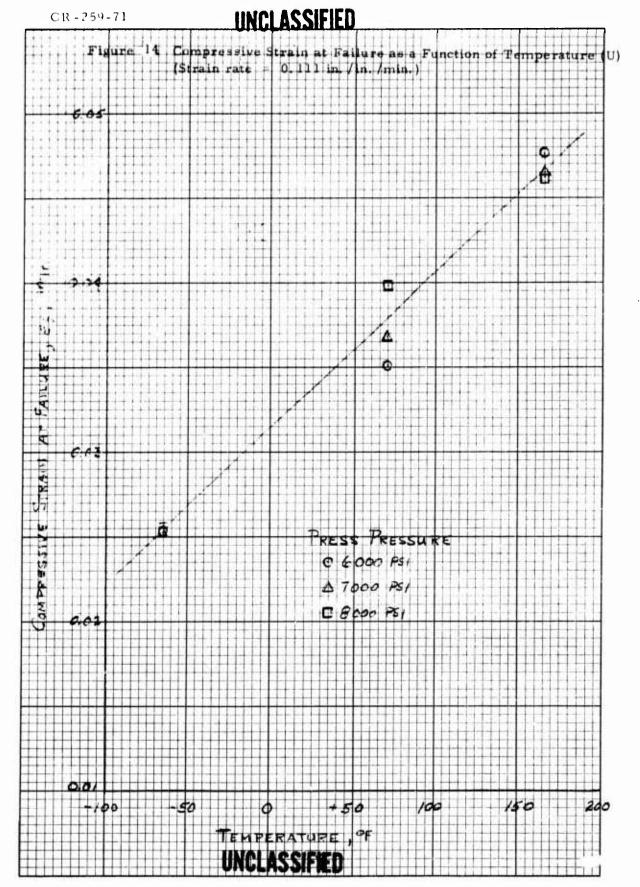
where ΔHa is the apparent activation energy for relaxation processes, see Reference (4).

(5) Density Versus Press Pressure (U)

(U) The density of propellant samples pressed at 5000, 6000, and 7000 psi was determined from the measured weight

Figure 13. Compressive Stress at Failure as Function of Temperature (U)
(Strain rate = 0.111 in./in./min.)

PRESS PRESSURE
⊖ 6000 PSI
△ 7000 PSI
⊡ 8000 PSI

COMPRESSIVE STRESS AT FAILURE, σ_f, PSI

4000

3000

2000

1000

-100   -50   0   +50   100   150   200

TEMPERATURE, °F
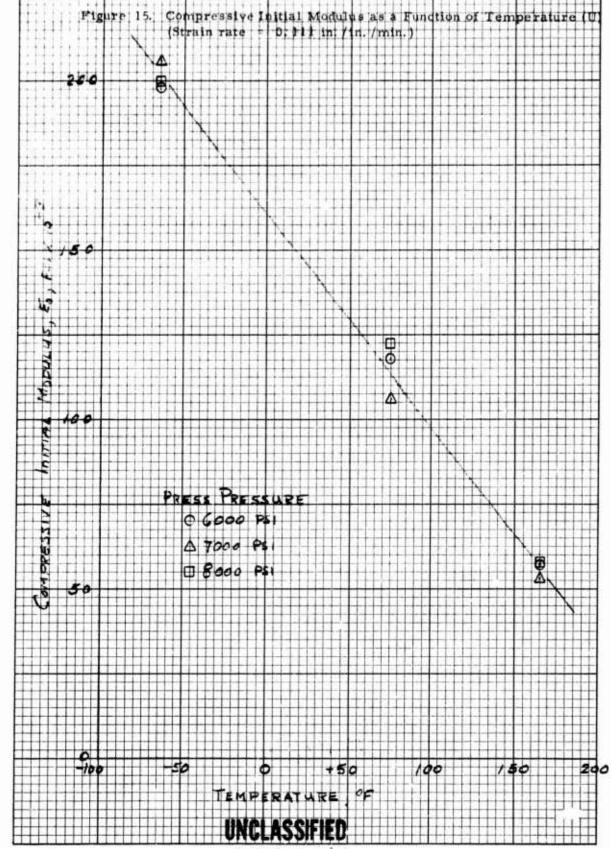
K·E 10 X 10 TO THE INCH 46 0703
7 X 10 INCHES   MADE IN U.S.A.
KEUFFEL & ESSER CO.

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Figure 14 Compressive Strain at Failure as a Function of Temperature (U)
(Strain rate = 0.111 in./in./min.)

PRESS PRESSURE
○ 6000 PSI
△ 7000 PSI
□ 8000 PSI

COMPRESSIVE STRAIN AT FAILURE, ε, in/in

TEMPERATURE, °F

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Figure 15. Compressive Initial Modulus as a Function of Temperature (U) (Strain rate = 0.11 in./in./min.)

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Figure 16 - Compressive Properties of Initial Modulus, Stress and Strain at Failure as Functions of Time Reduced to 70°F (U)

Figure 17.   Shift Factor Log a_T as a Function of Temperature (U)

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and dimensions of 0.6-inch diameter, 2.0-inch length cylinders. Five specimens were pressed at each pressure.

(U) Density and tensile property measurements are given in Table X. . Density increases slightly with increasing press pressure. Grains 0.5 inches in diameter and 1.5 inches in length which were pressed in the laboratory at 8000 psi were two percent higher in density than the three-inch diameter grains used for this study. The compressive strength of the three-inch diameter grains was 23 percent higher than that of the smaller diameter grains, however. It is not known why these differences exist, but it is suspected that it is due to the manner of sample preparation. The laboratory 0.5-inch by 1.5-inch samples were individually pressed, but the other samples were machined from 3.0-inch grains using a coring tool.

(U) Plots of density and compressive strength as functions of pressure for both size grains are given in Figure 18.

(6) Tensile Strength (U)

(U) The specimens used for determination of tensile strength are the same 0.6-inch diameter by 2.0-inch long dowels that were used for density determination. The specimens were bonded to metal end caps and subjected to constant strain-rate tensile loading along the longitudinal axis. The specimens were conditioned to $70^{\circ}F$ and tested with an Instron Tester at a strain-rate of 0.2-inch per minute.

(U) The tensile properties of propellant pressed at the four pressures 5000, 6000, 7000, and 8000 psi, are given in

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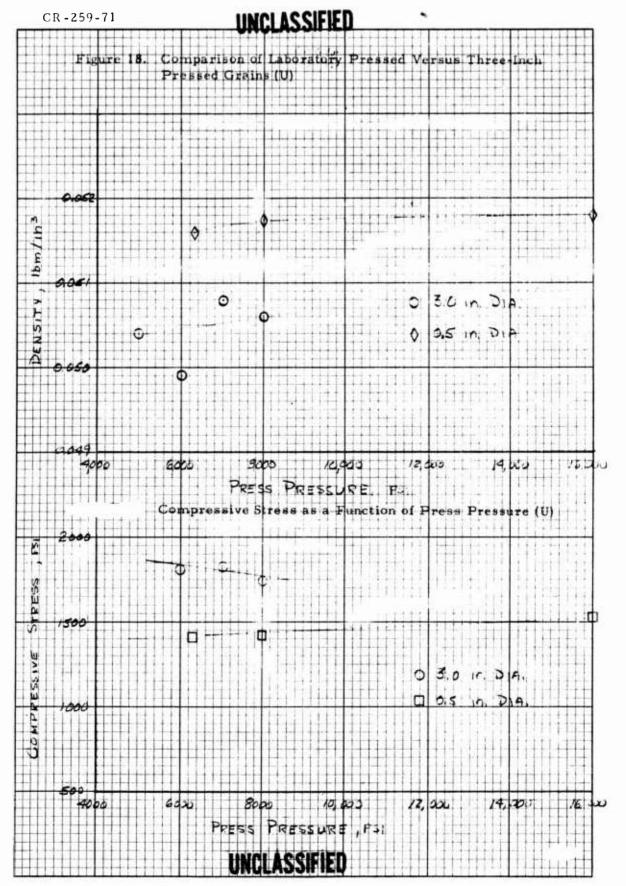
Table X - Density and Tensile Properties Of R-500 Propellant Pressed At Reduced Pressures (U)

Press Pressure (psi)	Stress at Failure (psi)	Strain at Failure (in./in.)	Initial Modulus (psi)	Density (lb./cu. in.)
5000	245	0.032	7200	0.0504
5000	263	0.043	6600	0.0505
5000	272	0.034	6000	0.0502
5000	---	-----	----	0.0505
5000	246	0.042	6200	0.0506
Average	257	0.038	6500	0.0504
6000	262	0.039	6600	0.0499
6000	226	0.036	6200	0.0496
6000	199	0.029	6800	0.0499
6000	260	0.038	7200	0.0501
6000	219	0.030	7200	0.0500
Average	233	0.034	6800	0.0499
7000	165	0.022	7600	0.0503
7000	244	0.039	6800	0.0512
7000	159	0.022	7200	0.0508
7000	236	0.028	8400	0.0501
7000	205	0.027	7600	0.0502
Average	202	0.028	7520	0.0505
8000	188	0.027	6600	0.0508
8000	246	0.030	8400	0.0509
8000	216	0.033	6600	0.0503
8000	219	0.035	5200	0.0502
8000	194	0.025	7300	0.0509
Average	213	0.030	6820	0.0506

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Figure 18. Comparison of Laboratory Pressed Versus Three-Inch Pressed Grains (U)

Compressive Stress as a Function of Press Pressure (U)

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Table X. Considerable scatter was obtained for the tensile properties and little or no correlation was obtained between the measured values of stress, strain, and modulus with density. The erratic tensile measurements are characteristic of pressed grains with a low binder content.

(7)   Coefficient of Linear Thermal Expansion (U)

(U) Thermal expansion was determined for four, 0.6-inch diameter, 2.0-inch length cylinders using a quartz tube dilatometer. The temperature of each specimen was increased from -65°F to +165°F at a rate of 1.8°F per minute. The specimen length was measured to within 0.0001 inch.

(U) A phase change of pressed R-500 propellant was discovered during the coefficient of thermal expansion tests. During the tests, it was noticed that the sample length decreased rather than increased at temperatures between 80 and 90°F. The coefficient of linear thermal expansion below and above the phase transition averaged 4.68×10^{-5} in./in./°F. Typical data for one of the four samples are plotted in Figure 19. A 0.25 percent reduction in length occurred at the phase transition and 1.84 calories per gram was absorbed. The phase change differential scanning calorimeter endotherm is shown in Figure 20.

(8)   Specific Heat (U)

*(U) Specific heat was measured for purified oxidizer (Grade III guanidine nitrate) from 50°C to 100°C for five samples. The Grade III material was tested because it

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Figure 19 - Coefficient of Linear Thermal Expansion Sample #1 (U)

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Figure 20. DSC Plot of Phase Transition (U)

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PHASE CHANGE

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TEMPERATURE °C

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was felt that more reliable data would be obtained from material having decreased impurities. The specific heat was determined by comparison with aluminum oxide (sapphire).

(U) The measured data are given in Table XI. The equation representing specific heat over this temperature range has the form:

Specific heat = 0.279 + 0.00152T,

where T is temperature in degrees centigrade.

(9)   Heat of Fusion (U)

(U) The heat of fusion of five samples was determined by differential scanning calorimetry. The area of the melt endotherm was measured for samples of known weight with a controlled heat input.

(U) A typical DSC melting point scan for R-500 propellant is shown in Figure 21. The values of heat of fusion for the five samples tested are 42.42, 41.16, 39.08, 40.69, and 41.99 calories per gram which give an average heat of fusion of 41.02 calories/gram.

(10) Autoignition Temperature (U)

(U) Two methods were used to determine autoignition temperature. The first method consisted of heating samples in a differential scanning calorimeter at three rates, i.e., 5°, 40°, and $80^{\circ}C$, per minute until decomposition occurred. The time from $30^{\circ}C$ to the exotherm peak as well as the time and temperature of the onset of decomposition was measured for five samples at each heating rate.

Table - XI
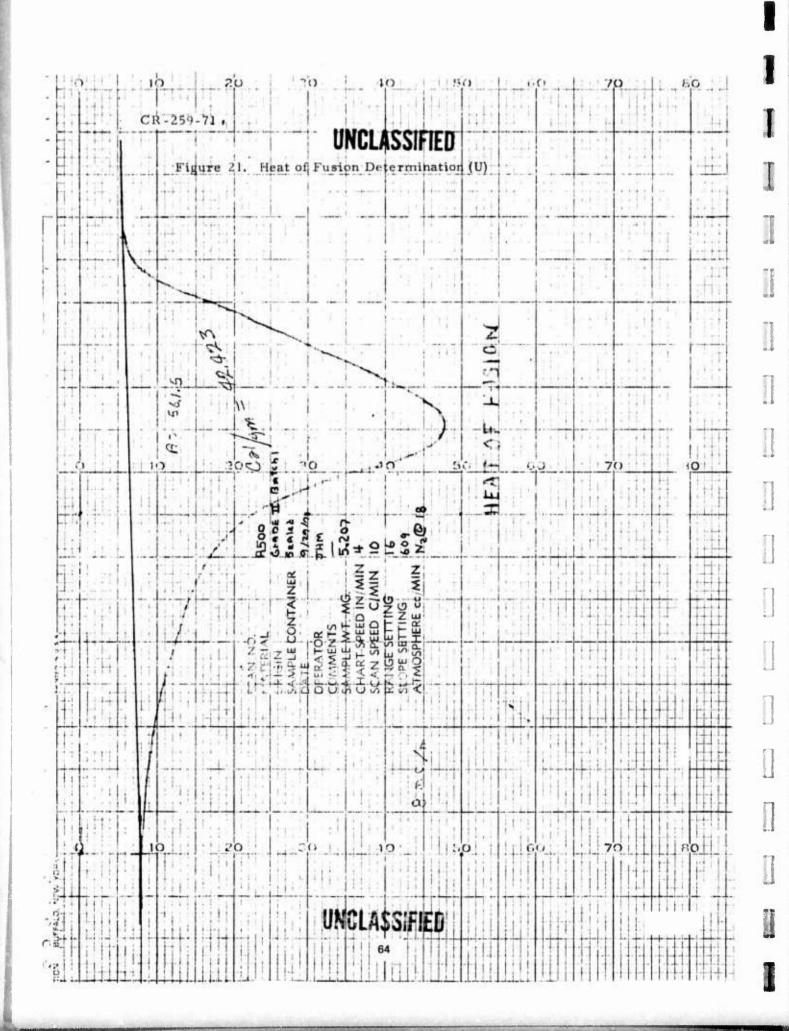
Specific Heat of R-500 (U)

Sample Temperature, °C	Specific Heat, calories per gram per degree					
	50	60	70	80	90	100
Scan Number 1	0.375	0.363	0.387	0.457	0.471	0.483
2	0.385	0.358	0.364	0.370	0.385	0.404
3	0.365	0.375	0.409	0.408	0.385	0.413
4	0.364	0.347	0.384	0.319	0.426	0.433
5	0.371	0.383	0.408	0.401	0.420	0.415
Average	0.363	0.365	0.390	0.391	0.417	0.431

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Figure 21. Heat of Fusion Determination (U)

HEAT OF FUSION

$A = 561.5$

$Cal/gm = 82.923$

SCAN NO.	
MATERIAL	A500
ORIGIN	Grade II Batch
SAMPLE CONTAINER	Sealed
DATE	9/22/23
OPERATOR	JHM
COMMENTS	
SAMPLE WT. MG.	5.207
CHART-SPEED IN/MIN	4
SCAN SPEED C/MIN	10
RANGE SETTING	16
SLOPE SETTING	609
ATMOSPHERE cc/MIN	N₂ @ 18

64
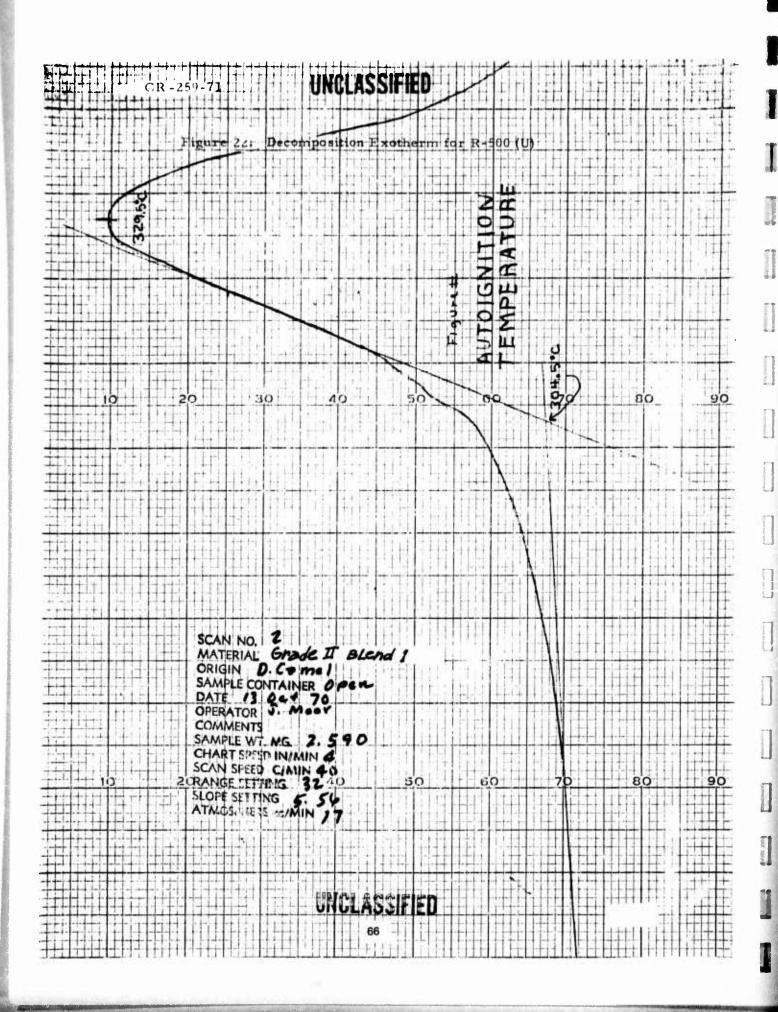
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(U) The second method consisted of measuring the time to decomposition of samples placed in a constant temperature bath, see references(5) and(6). Fifteen tests were made with samples sealed in copper tubes 0.25-inch in diameter and 1.5-inch long. The tubes were immersed in a woods metal bath and the time from immersion to ejection of the end cap of the tube due to internal pressurization was measured.

(U) A typical differential scanning calorimeter scan for the decomposition exotherm of R-500 is shown in Figure 22. The temperature data for initiation of decomposition and maximum heat evolution are given in Table XII. The time from $30^{\circ}C$ to decomposition is plotted as a function of reciprocal absolute temperature in Figure 23.

(U) The autoignition temperature by the closed cup method gave a 5-second value of $355^{\circ}C$ and a 0.1-second value of $453^{\circ}C$. The data are given in Table XIII.

(11) Impact Sensitivity (U)

(U) Impact sensitivity was measured for 0.1-gram samples with a drop hammer tester. Samples were placed on an anvil and struck with a 5-kilogram weight released from a known height above the anvil. Twenty-five tests were made.

(U) No fires were obtained in 25 drop hammer tests with a 5-kilogram weight dropped from 352 centimeters which is the maximum height for the instrument.

(12) ICC Classification (U)

(U) The ICC classification for the oxidizer as listed

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Figure 24. Decomposition Exotherm for R-500 (U)

SCAN NO. **2**
MATERIAL **Grade II Blend 1**
ORIGIN **D. Comel**
SAMPLE CONTAINER **Open**
DATE **13 Oct 70**
OPERATOR **J. Moor**
COMMENTS
SAMPLE WT. MG. **2.590**
CHART SPEED IN/MIN **4**
SCAN SPEED C/MIN **40**
RANGE SETTING **32** 40
SLOPE SETTING **5.54**
ATMOS. CC/MIN **17**
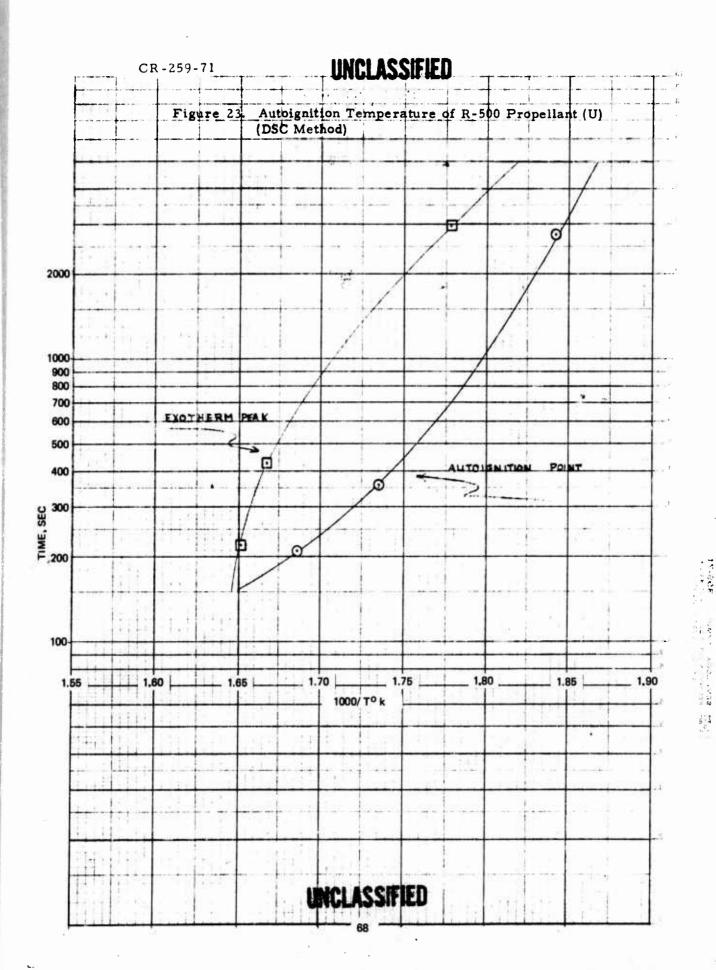
Table XII - Autoignition Temperature DSC Analysis (U)

Heating Rate °C/min	Autoignition Temperature °C	Explosion Temperature °C
5	274	290
5	269	288.5
5	261	289.5
5	276	288.5
5	269	290
Average	269.8	289.3
	$1000/T^{\circ}k = 1.842$	$1000/T^{\circ}k = 1.778$
40	300	321.5
40	304	331
40	304	329
40	304.5	328
40	305	323.5
Average	303.5	328.6
	$1000/T^{\circ}k = 1.735$	$1000/T^{\circ}k = 1.682$
80	326	---
80	319	334
80	317	339
80	317.5	343
80	323.5	347
Average	320	332.6
	$1000/T^{\circ}k = 1.686$	$1000/T^{\circ}k = 1.651$

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Figure 23. Autoignition Temperature of R-500 Propellant (U)
(DSC Method)

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Table XIII - Autoignition Temperature Explosion Temperature Method (U)

Time, Seconds	Temperature, °C	1000/T°k
2.7	371	1.553
3.3	353	1.597
3.4	359	1.582
4.1	370	1.555
6.0	362	1.575
6.1	344	1.621
6.2	338	1.637
9.0	338	1.637
9.7	343	1.623
9.9	336	1.642
10.2	345	1.618
10.3	335	1.645

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in T. C. George's Tariff No. 23, part 172.5, is
oxidizing material (yellow label).

(13) Long Term Aging Effect (U)

(U) The objective of this effort was to determine
the effects of long term aging on the burning rate and
tensile properties of R-500 propellant. This was
accomplished by placing control samples of propellant
in conditioning at two different temperatures and testing
portions of the samples at specified time intervals.

(U) Eighteen, 3-inch diameter propellant grains
from one batch of R-500 propellant were pressed in
accordance with the established procedure. The grains
were dimensionally inspected, radiographically inspected
and placed in sealed containers. Nine containers were
placed in $80^{\circ}F$ temperature controlled conditioning and
nine in $180^{\circ}F$. Thirty samples, from the same batch of
R-500, machined into compressive specimens were also
placed into storage at the same time as the propellant
grains. These samples were X-rayed and placed in sealed
containers. Fifteen containers were placed in $80^{\circ}F$ temp-
erature controlled conditioning and 15 in $180^{\circ}F$.

(U) The aging effect on burning rate was determined
by testing the 3-inch diameter propellant grains in the 3-
inch diameter test motor. The timing for removal of the
grain from conditioning was conducted in the sequence
shown in Table XIV. At the specified time intervals, the
required number of grains were removed from storage,
X-ray inspected and placed in conditioning at $70^{\circ}F$ in
preparation for testing. The grains were static test
evaluated at a constant K_n with the catalyst in contact with

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the propellant surface.

Table XIV Long Term Aging Test Sequence (U)

Aging Conditioning Temperature (°F)	3-Inch Motor Test		Compressive Tensile Coupons	
	No. Samples to test	No. Weeks Conditioning	No. Samples to Test	No. Weeks Conditioning
80	3	4	5	4
80	3	12	5	12
80	3	26	5	26
180	3	1	5	1
180	3	4	5	4
180	3	12	5	12

(U) The aging effect on compressive properties of R-500 was determined by testing Compressive specimens in the propellant laboratory. Specimens were machined from the propellant samples after the specified storage time and temperature requirements of Table XIV were met. At the specified times, five samples were removed from conditioning, X-Ray inspected, specimens prepared, and the specimens placed into conditioning at $70°$ F in preparation for testing. The five specimens were compressive tested using an Instron Tester at a crosshead speed of 0.2 inches per minute. The data obtained in these tests were:

o   Compressive strength

o   Strain

o   Compressive Modulus

(U) Each of the above data items was charted as a function of aging time at each temperature and is shown in Figures

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24, 25, and 26 respectively. The burning rate constant at
the two conditioning temperatures is shown in Figure 27.

(U) The compressive strength of the samples conditioned
at 80^OF demonstrated a reduction in strength from 0-4 weeks
conditioning but by the 12th week the strength was greater
than the initial value with very little change occurring between
12 and 26 weeks. The samples conditioned at 180^OF demon-
strated improved strength with time over a period of 1 to 12
weeks. After 12 weeks, the strengths of propellant conditioned
at 180^OF and 80^OF were equal. The strain (see Figure 25) of the
samples stored at both 180° and 80^OF showed improvement with
time over the periods evaluated. The strain of those samples
stored at 180^OF was lower than that of the samples stored at 80^OF.

(U) The compressive modulus (See Figure 26) of samples
stored at both temperatures experienced decreases in the
period of 0 to 4 weeks but increased to values greater than
the initial modulus at the 12 week period. The modulus of the
samples stored at 180^OF was approximately the same as that
of the samples stored at 80^OF for the first 4 weeks but was
significantly higher after the 12 week period.

The burn rate constant (See Figure 27) of propellant
samples stored at both temperatures demonstrated significant
degradation in the period between 0 and 4 weeks. After this
period of time the burn rate constant degraded much less up
to the 26 week period.

c. Conclusions (U)

(1) General (U)

(U) The ballistic properties of R-500 propellant were
characterized between the pressures of 250 and 800 psia in
vertical tests and data have been generated for use in designing

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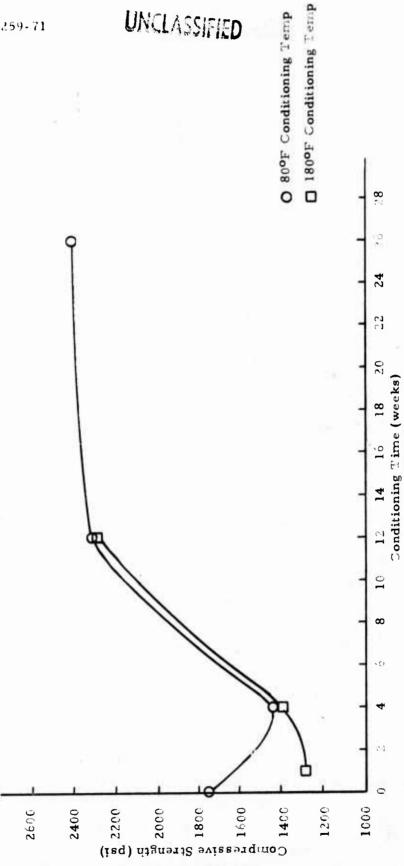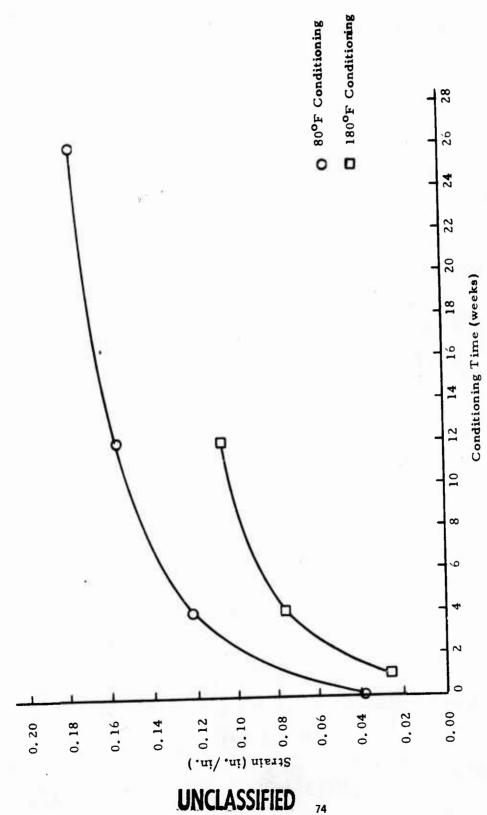
Figure 24 - Compressive Strength of R-500 Propellant as a Function of Conditioning Temperature and Time (U)

Figure 25 - Strain of R-500 Propellant as a Funct   of Conditioning Temperature and Time   (U)
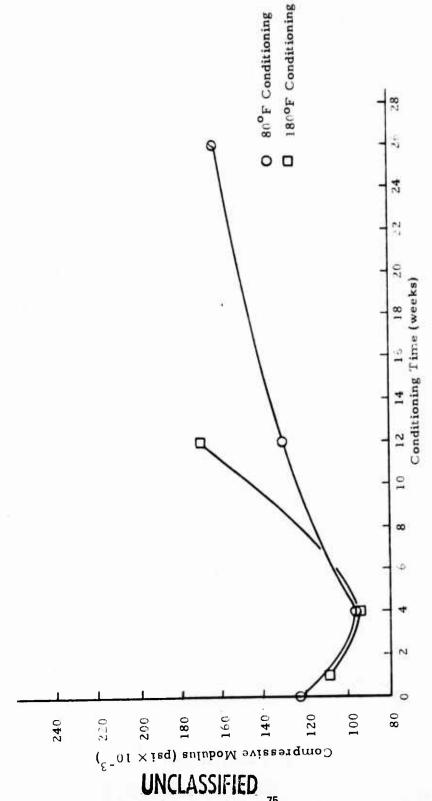
Figure 26 - Compressive Modulus of R-500 Propellant as a Function of Conditioning Temperature and Time (U)
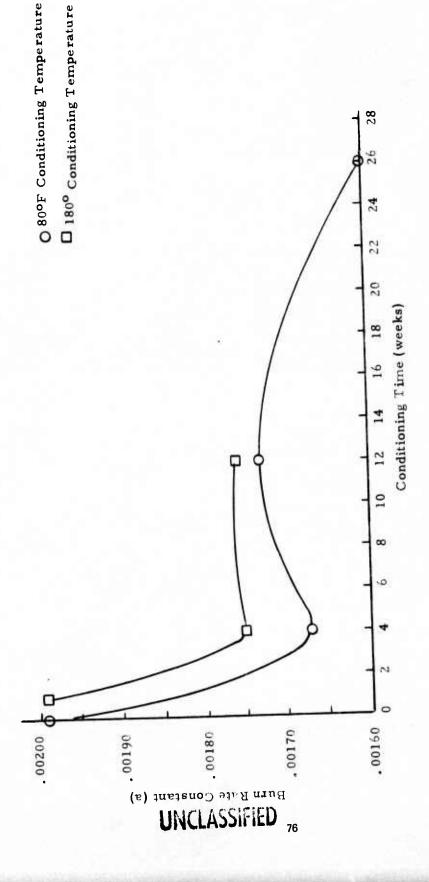
Figure 27 - Burn Rate Constant as a Function of Conditioning Temperature and Time
R-500 Propellant

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future propulsion systems between -65 and 160°F. Two horizontal tests were also performed and the attitude did not seem to effect the ballistic performance. The physical properties of R-500 propellant were characterized between -65 and $+165^{\circ}$F.

(2) Burn Rate Sensitivity (U)

(U) The sensitivity of R-500 burn rate to temperature at a constant pressure (σ p) varied between 0.13 and $0.20\%/^{\circ}$F over the tested pressure and temperature ranges. These values are comparable to those of conventional composite propellants. The pressure sensitivity to temperature at a constant K_n (π k) varied from 0.023 to $0.40\%/^{\circ}$F over the tested pressure and temperature range. The low value of π k ($0.023\%/^{\circ}$F) did not correspond to the σ p and burn rate-pressure exponent. The relationship of the three parameters is described in the following equation:

$$\pi_k = \frac{\sigma_p}{(1 - n)} ,$$

where n = burn rate-pressure exponent.

(U) For the π k to be of smaller value than the σ p, the burn rate-pressure exponent would have to be negative. This was not the case. The problem is the lack of K_n-pressure data at $+160^{\circ}$F as only four motors achieved equilibrium operation. Additional testing was not recommended since the Northrop Carolina constant pressure operating demand gas generator is not sensitive to K_n or πk.

(3) Burn Rate Reproducibility (U)

*(U) Burn rate reproducibility tests were performed with Grades I, II, and III guanidine nitrate and it was determined that the purity of the guanidine nitrate did not have a significant

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effect on ballistic performance of R-500 propellants. There-
fore, the purity of guanidine nitrate was not a critical property
requiring close tolerance control.

(4)   Physical Properties (U)

(U) The compressive properties of R-500 propellant are
comparable to those of other compression molded propellants.
The compressive properties were determined over press
pressures from 6000 psi to 8000 psi and temperatures from -65
to +165°F. The press pressure did not have a significant effect
on compressive properties or density. The compressive
strength responded as expected to temperature, increasing as
the conditioning temperature was reduced. Other tests performed
on laboratory samples also indicated no effect of press pressure
on density but there was an effect on tensile strength. The
tensile strength decreased 17 percent as the press pressure was
increased from 5000 to 8000 psi. Therefore, depending on
the application, the press pressure may need to be closely
controlled.

(U) The constant strain rate compressive properties were
further characterized by time-temperature superposition. Poor
alignment of the data was obtained using the Williams Landel and
Ferry equation for the dimensionless shift factor a_T. This is
probably due to the shift factor not being applicable because R-500
propellant is not viscoelastic.

(5)   Thermal Properties (U)

(U) A phase transition, for R-500 propellant, was observed
between the temperatures of +80 and +90°F. In this temperature
range the propellant experienced a negative linear coefficient
of thermal expansion. Below and above this temperature range
the coefficient is comparable to that of other pressed propell-
ants. The phase transition was verified by differential scanning

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calorimeter testing.

(U) Since the phase transition is in a probable operating temperature range, it was recommended that further physical property tests and motor tests be performed to ascertain the effect, if any, on the physical and ballistic properties of R-500. Additional testing was not approved.

(U) The specific heat of R-500 propellant is typical for conventional composite propellants. The heat of fusion cannot be compared because conventional propellants do not experience the melt phase which is characteristic of R-500. The autoignition temperature was much higher than that of conventional propellants. This makes the propellant safer to handle, store, and manufacture, but may cause it to be more difficult to ignite.

(6) Impact Sensitivity (U)

(U) The impact sensitivity of R-500 is less than conventional propellants which is also indicative of handling and manufacturing safety.

(7) Long Term Aging Effects (U)

(U) The long term aging effects of R-500 propellant have been characterized at $80^{\circ}F$ over a period of 26 weeks and at $180^{\circ}F$ over a period of 12 weeks. The following conclusions have been made based on the tests performed.

a) The compressive strength of R-500 propellant at both conditioning temperatures is not degraded with storage time.

b) The strain, at constant crosshead speed, of R-500 propellant is increased with storage time at both temperatures.

c) The compressive modulus of R-500 is not degraded over extended storage periods at the tested temperatures.

d) The burn rate constant of R-500 changes significantly in the first 0 to 4 weeks period after processing. This will have a significant effect on ballistic performance of R-500 propellant and should be more thoroughly character-ized to determine the cause.

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5. INHIBITOR DEVELOPMENT (U)

a. Introduction (U)

(U) The objective of this study was the development of an inhibitor for R-500 propellant. The specific goals for the R-500 inhibitor were:

- A bond strength of at least 75 psi between the inhibitor and the R-500 grain.
- A material that will restrict burning on all propellant surfaces, except those designated by the ballistic design.
- A material that is chemically compatible with R-500 propellant and the catalyst so that inhibitor decomposition products will not poison the catalyst during motor operation.
- A material that will produce primarily gaseous products rather than a char that could obstruct catalyst movement during motor operation.

(U) The pressed grain inhibitor development task consisted of the selection of candidate inhibitors; conducting chemical compatibility, bond strength combustion, and char formation tests; characterizing the mechanical properties of two inhibitors; making an inhibitor selection; and then performing long-term aging tests.

b. Selection of Inhibitor Candidates (U)

*(U) The candidate binders were selected on the basis of known compatibility with guanidine nitrate, inertness on aging, and high elasticity. Two epoxy binders, EC-2216 and Epon 812, were considered, but rejected because of low elasticity. A carboxy-terminated polybutadiene, HX-434, and a carboxy-terminated polyester, F 17-80, were selected based on results obtained in the castable propellant work. Both are compatible

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with guanidine nitrate when the polybutadiene is cured with either ERL-0510, HX-868, or MAPO and the polyester is cured with DEN 438.

*(U) A filler in the inhibitor can reduce char formation during combustion and can increase the inhibitor viscosity, which aids in the application of the inhibitor to the outside grain surface prior to insertion in the insulation tube. Carbon black, ammonium sulphate, asbestos floats, ammonium phosphate, and ammonium chloride were considered as fillers, but were rejected because of the possibility that these materials might form decomposition products which would poison the catalyst. Guanidine nitrate was chosen for a filler because its decomposition products will be identical to those of the propellant. Selected binders containing less than 50 percent by weight of guanidine nitrate will regress at a slower rate than pure guanidine nitrate during motor operation.

c.   Inhibitor Evaluation and Selection (U)

*(U) Differential scanning calorimeter tests were run on mixtures of HX-434 with Grade II guanidine nitrate and on F 17-80 mixed with Grade II guanidine nitrate. The first reaction occurred at the melting point of guanidine nitrate, and the only other event was a large exotherm above 300°C which was interpreted to be the decomposition of guanidine nitrate. It was concluded that the two binders were compatible with guanidine nitrate.

(U) The tensile bond strengths of the candidate inhibitors to RPD and to R-500 were measured by adhesion cup tests. The results are given in Table XV. Both the HX-434 cured with HX-868 and the polyester gave bond strengths to R-500 which

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TABLE XV - INHIBITOR TENSILE BOND STRENGTH (U)

Inhibitor Composition (Weight %)	Shore A Hardness	Tensile Strength (psi)			
		Inhibitor/RPD-150	Inhibitor/RPD-110	Inhibitor/R-500	Inhibitor/R-501
HC-434 (56.90) MAPO (2.27) ERL-0510 (0.83) Guanidine Nitrate (40.00)	42	62		$36^{(1)}$	$16^{(1)}$
HC-434 (55.41) HX-868 (4.59) Guanidine Nitrate (40.00)	37	$38^{(4)}$		$77^{(1)}$	--
F 17-80 (47.84) DEN 438 (12.16) Guanidine Nitrate (40.00)	57	$52^{(5)}$		$106^{(1), (3)}$ $75^{(2), (3)}$	--

(1) Inhibitor thickness: 0.1 inch
(2) Inhibitor thickness: 0.01 inch
(3) Inhibitor-to-steel failure
(4) RPD-110, uncured
(5) Failure in inhibitor

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exceeded 75 psi. The bond strength with the polyester exceeded the inhibitor's stress capability. The low bond strength of the HC-434/HX-868 inhibitor to RPD is believed to be due to the type of RPD (uncured - 110) used in that test rather than a characteristic of the inhibitor.

(U) Char characteristics of the inhibitors were investigated with three types of tests: (1) open flame tests, (2) bench catalyzed test of three-inch diameter grains in RPD cups, and (3) motor tests with three-inch diameter grains. During the torch tests the inhibitors without a filler melted, coating the propellant surface. This melting was eliminated by the addition of filler. Bench test results are summarized in Table XVI. Each inhibitor left some char on the inside of the RPD cup. The polyester inhibitor left no char on the catalyst and less char on the cup than the polybutadiene inhibitors. The polyester inhibitor left more char than the HC-434/HX-868 inhibitor in the three-inch diameter test results. In both bench and motor tests, the inhibitor containing HC-434 cured with MAPO and ERL-0510 produced more char than the other inhibitors.

*(U) The HC-434 cured with MAPO and ERL-0510 inhibitor system was eliminated because of the char that it produced. One gallon mixes were made of the HC-434/HX-868 and the F 17-80/ DEN-438 inhibitors with 40 percent Grade II guanidine nitrate for further bond tests and to determine the mechanical properties of the inhibitors at -65°, 70°, and $165^{\circ}F$.

(U) Table XVII lists bond strength, tensile, and elongation data. In all cases bond failure occurred at the inhibitor to R-500 bond. The stress and elongation capability of the polybutadiene system exceeds that of the polyester at each temperature,

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TABLE XVI - CHAR BENCH TESTS* (U)

Inhibitor Composition (Weight %)	Char Condition	Catalyst Condition
HC-434 (56.90) MAPO (2.27) ERL-0510 (0.83) Guanidine Nitrate, Grade III (40.00)	Firm char adhering to cup	Char on catalyst
HC-434 (55.41) HX-868 (4.59) Guanidine Nitrate, Grade III (40.00)	Heavy, soft char adhering to cup	Char on catalyst
F 17-80 (47.84) DEN 438 (12.16) Guanidine Nitrate, Grade III (40.00)	Very little firm char adhering to cup	Clean catalyst

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TABLE XVII - INHIBITOR EVALUATION DATA (U)

	Polybutadiene	Polyester
Binder Type		
Prepolymer	HC-434	F 17-80
Curative	HX-868	DEN 438
Guanidine Nitrate Compatibility		
D.S.C.	Acceptable	Acceptable
Aging 30 days at 80°C	Acceptable	Acceptable
Bond Strength to R-500 (psi)	100	146
Mechanical Properties		
Maximum Stress (psi)		
-65°F	360	3900
+70°F	100	94
+165°F	60	56
Strain at Maximum Stress (in./in.)		
-65°F	2.60	0.04
+70°F	3.70	0.40
+165°F	2.40	0.28
Char Formation		
Bench Tests	Acceptable	Acceptable
Motor Tests	Acceptable	Acceptable

particularly at -65°F. For applications where temperature is controlled between 60 and 100°F, the polyester inhibitor is acceptable and may be preferable because of its higher bond strength to R-500 propellant.

(U) The polybutadiene-inhibitor was selected as the inhibitor for the aging studies because of its superior properties over the temperature range of -65°F to +165°F.

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6. CATALYST DEVELOPMENT (DEACTIVATION) (U)

a. General (U)

(U) An investigation was conducted to determine the cause and solution for catalyst deactivation experienced in certain motor tests of the Demand Gas Generator program.

(U) Emission spectrographic analyses of propellant and catalyst samples indicated that the concentrations of silicon and sodium compounds in the R-500 propellant were related to catalyst deactivation in both three-inch and twelve-inch diameter motor tests, and that the source of these impurities was the propellant raw material. The introduction of known quantities of silicon dioxide and sodium fluoride into otherwise relatively pure propellant confirmed these analyses in three-inch diameter motor tests. It was shown that motor equilibrium pressure for continuously catalyzed tests and propellant burning rate are functions of the concentration of incombustible propellant impurities as measured by residual ash content, i.e.

at K_n = 1104

$\ln P_{eq.}$ = 6.314 - 0.827 $\times$ percent residual ash

and

at $P_{eq.}$ = 500 psia

$\ln r_b$ = -2.489 - 4.878 $\times$ percent residual ash

(U) Kinetic rate constant determinations for the thermal decomposition of the propellant showed that the impurities are non-catalytic and reduced the reaction rate by covering the active catalyst surface. The catalyst surface area was not significantly reduced by the coating. Long duration twelve-inch diameter motor tests indicated that the degree of deactivation approached a limiting value for a given impurity content during motor operation.

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(U) It was recommended that R-500 propellant raw material be purified prior to use to reduce the concentration of incombustible impurities to a level of 0.03 percent or less.

b. Conclusions (U)

(U) Specific conclusions based on the standard catalyst bed deactivation study are listed below.

- (U) The R-500 propellant raw material contains inorganic impurities such as silica, sodium silicate, etc. which are stable liquids or solids at motor operating temperatures.

- (U) These impurities coat the bottom surface of the catalyst bed screen in contact with the propellant during motor operation.

- (U) The impurities are noncatalytic and reduce the activity of the catalyst by covering active sights which otherwise would catalyze the thermal decomposition of the propellant.

- (U) Contamination of the catalyst reduces the catalyzed burning rate of the propellant. The reduction in burning rate is a function of the concentration of such impurities in the propellant.

- (U) For a given propellant impurity level, the degree of catalyst deactivation approaches a limiting value with motor operating time which indicates that an equilibrium is attained between the impurities on the catalyst and those in the propellant melt layer.

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7.   IGNITION SYSTEM DEVELOPMENT (U)

  a.   Introduction (U)

    (U) The objective of the ignition system development portion
of this program was to develop an ignition system for the Demand
Gas Generator which would result in grain ignition, catalyst
heating, and chamber filling within a reasonably short period of
time.

    (U) Quantitative goals defining a successful ignition were not
set during the program because ignition of a propellant surface
in contact with a catalyst bed introduces a heat sink resulting in
nonsteady state burning of that propellant surface.   This introduces
thermal problems heretofore unencountered in solid propellant
rocketry.   The definition of a successful ignition was determined
as a sequence that provided adequate heating of the catalyst bed
and main propellant and which yielded steady state catalytic burning
of the main propellant shortly after completion of the ignition phase.

    (U) Although the principal ignition problem, chamber pressure
perturbations during initial stages of R-500 burning, was known to
be caused by insufficient heating of the catalyst bed, positive ana-
lytical correlation was not made until midway through the program.

    (U) Significant accomplishments were made in understanding,
correlating, and calculating ignition phenomena during the program.

  b.   Approach (U)

    (U) The ignition system development approach included three
major efforts.

    (U) First an analytical study was made on three candidate
igniter types, electrical pyrotechnic, and pyrogen.   The analytical

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investigation of three ignition methods included heat flux re-
quired to raise the catalyst and propellant temperatures to igni-
tion levels within various time intervals, mass flux required to
perform at least partial chamber filling within various time in-
tervals, coating and contamination effects on the catalyst, ignition
reliability, external electrical power requirements, ease of
fabrication and implementation weight, and ignitability under near
vacuum conditions (300k-feet altitude).

(U) The analytical investigation concluded with the selection
of two candidate ignition methods for further evaluation and tests.
The selected systems and reasoning for their selection was sub-
mitted to the procuring contracting officers for approval.

(U) Secondly, the two selected ignition methods were further
investigated by design and testing of three-inch diameter test vehicles.
The standard catalyst and propellant were used in these tests and
the catalyst was held in contact with the grain. Chamber pressure
and flame temperature versus time, propellant b rning rate, and
current requirements to attain ignition were measured and evaluated
to determine the ability of the ignition technique to meet the design
objectives. Catalyst beds were inspected and burning rates were
compared to historical burning rates to determine contamination
effects.

(U) Based on this evaluation, one ignition technique was selected,
with procuring contracting officer approval, for further evaluation
in twelve-inch diameter tests.

(U) The third major effort of the ignition system development
approach was the twelve-inch diameter test series. Chamber pres-
sure and temperature versus time, propellant burning rate, and

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current requirements to attain ignition were measured to determine the ability of the selected system to meet design objectives. The catalyst beds were inspected and burning rates were compared to historical data to determine contamination effects.

(U) This approach was kept intact throughout the program, but the uniqueness of the transient catalytic burn rate of the base propellant brought about by an insufficiently hot catalyst bed resulted in the addition of six three-inch diameter tests after the "Demand Gas Generator Ignition System Selection Report", Reference (9), was completed. The number of twelve-inch diameter ignition tests increased from four to six.

c. Candidate Ignition System Analyses (U)

(U) The initial phase of the ignition development was the ignition analyses during which three types of ignition methods were analytically investigated. These methods were electric, pyrotechnic and pyrogen.

(U) The electrical method study model consisted of an electrical heating element designed into the catalyst bed to perform the function of catalyst heating. The hot catalyst then heated the grain, causing grain ignition and chamber filling resulted. The heating element was assumed powered from a source external to the Demand Gas Generator.

(U) The pyrotechnic method consisted of an external pyrotechnics initiator and propellant contained within the combustion chamber of the Demand Gas Generator. Electrical initiation was

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used. Combustion of the pyrotechnic and propellant material provided catalyst and main grain heating, chamber filling, and grain ignition.

(U) The pyrogen igniter consisted of an electrically initiated pyrotechnic and/or propellant material contained in a combustion chamber separate from the Demand Gas Generator combustion chamber. The combustion products exhausted from the pyrogen into the gas generator causing chamber filling and simultaneous heating of the catalyst bed and propellant surface to the catalytic ignition temperature.

(U) The evaluation criteria for the ignition methods fell into three categories: 1) envelope (weight and volume), 2) performance (delay time, rise time, and contamination), 3) design considerations (power requirements, maintenance and upkeep, ease of fabrication, compatibility, and cost).

(1)   Thermal Analyses (U)

(U) To attain equilibrium operation, the propellant grain surface must be raised to its equilibrium temperature (somewhat near autoignition temperature), the temperature profile proceeding the regressive burn surface must be constant, the catalyst must be raised to the reaction temperature, and the combustion chamber must be pressurized to its operation level. A change in any parameter upsets the net heat flux at the propellant surface and a transient burning rate would exist.

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(U) To initiate system operation, the propellant surface must be heated to its autoignition temperature and the heated catalyst bed must be brought into contact with this surface. Chemical reactions then begin and equilibrium operation eventually is attained. To reduce the time required to attain equilibrium operation, the functions of chamber filling and catalyst heating can be accomplished by the ignition phase rather than the system reaction.

(U) The thermal analyses considered three factors in grading the relative merits of the candidate methods.

1.   The quantity of heat required for the propellant and catalyst bed

2.   The quantity of heat available from the ignition system

3.   The rate at which heat could be transferred between the heat sources and the heat sinks, i.e. propellant and catalyst bed.

(a)   Quantity of Heat Required (U)

(U) The quantity of heat required to affect steady state catalysis is the sum of the heats required to raise the propellant catalyst bed to the temperatures necessary for a catalytic reaction.

(U) External heating of the propellant causes the temperature in the vicinity of the surface to rise. As the heating process continues, chemical reactions begin and replace the external heat source as the controlling stimulus. At some point in this process, ignition occurs

although this is not universally defined.

(U) Ignition models may be broadly divided into two types, i.e. 1) those which consider the propellant an inert solid, and 2) those which consider chemical reactions within the solid, on the surface, or in the gas phase adjacent to the igniting surface. The basic model of both model types is:

$$\rho \, Cp \, \frac{dT}{dt} \;=\; k \, \frac{d^2 T}{dx^2} \;+\; B \, (e)^{-\frac{E}{RT}} \qquad \text{Eq. (a)}$$

where:

ρ	=	density	B	=	coefficient
Cp	=	specific heat	E	=	activation energy
k	=	thermal conductivity	R	=	gas constant
T	=	temperature	e	=	logarithmic constant
t	=	time	$B(e)^{-\frac{E}{RT}}$	=	exothermic reaction term

(U) Solving the inert form of Equation (a) in terms of the surface temperature (at $x = 0$) and assuming constant surface heat flux yields:

$$q \, \dot{q} \;=\; \pi \, k \, \rho \, Cp \, (Ts - Ti)^2 / 4 \qquad \text{Eq. (b)}$$

where:

$$\dot{q} \;=\; -k \, \frac{dT}{dt} \, , \quad \text{heat flux}$$

q = heat content per unit area

T_s = final surface temperature

T_i = initial surface temperature

(U) For a given surface temperature rise, the product of energy stored in the solid and the heat flux is constant, and the time required to achieve this product may be calculated by an equation of the form:

$$T_{ign} = \psi k \rho C_p (T_s - T_i)^2 / (\dot{q})^2 \qquad \text{Eq. (c)}$$

where:

ψ = $\frac{\pi}{4}$ for $T_{ign} >> T_s$

t_{ign} = time to ignition

T_{ign} = temperature of ignition gases..

(U) Graphical representation of Equation (c) is presented in Figure 28. It should be noted that Equations (a), (b), and (c) are independent of the mechanism causing heat flux, be it radiation from an electrical wire grid, convection of pyrogen gases, or conduction from a hot catalyst bed.

(U) The heat required to raise the catalyst bed to an acceptable level is established by a simpler equation, because there is not a large temperature drop from the surface of each wire to the centerline. The individual wires of the screen increase uniformly in temperature according to the following equation:

$$q = W_t C_p (T_F - T_i).$$
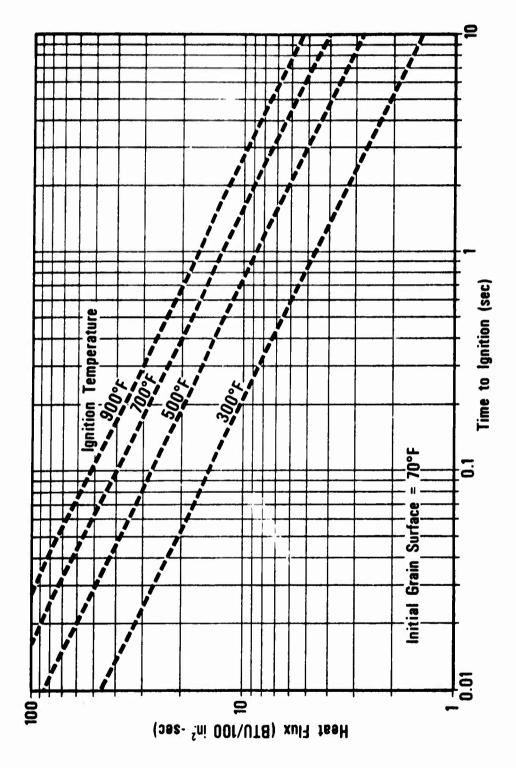
Figure 28 -   Heat Flux vs Time To Ignition (U)

where:

q = quantity of heat

W_t = weight of screen $\sim$ 0. 205 lb_m per 100 in.^{2}

Cp = specific heat of the screen $\sim$
0. 12 BTU/lb_m ^{o}F

Ti = initial temperature of the screen

T_F = final temperature of the screen.

(b) Available Heat (U)

(U) Heat available from the pyrotechnic ignition system comes from the initial pyrotechnic charge. used to pressurize the gas generator and ignite the overlay propellant. The conventional overlay propellant is used to further heat the catalyst bed. The amount of ignition mix used to perform these requirements is a function of the design chamber pressure, the volume-to-surface ratio of the gas generator, and thermodynamic properties of the pyrotechnic charges.

(U) Knowing the weight and heat content of the pyrotechnic charges to yield particular chamber pressures of specific chamber design configurations, and using the heat flux-time data to ignite propellants (given in Figure 28), it is possible to relate ignition time as a function of chamber design and pyrotechnic charge type and weight. The complete parametric investigation may be found in Reference (7).

(U) Similar to the approach used in the preceding paragraph, an analysis may be made on the pyrogen system.

(U) Heat available from the electrical ignition method and the time required to heat the catalyst bed screens are functions of current through, and voltage drop across, the heating element. The time required to heat the catalyst bed to the same temperature used in the pyrotechnic and pyrogen methods is 51 seconds with thirty amperes and 24 VDC.

(U) The propellant may also be ignited by applying a hot catalyst bed directly to the propellant surface. The primary mode of heat transfer is conduction through the intermittent surface contact. Analytical prediction methods are not reliable although most studies include loading pressure, surface irregularity, orientation, interface temperature, and material ductility or elongation functions. An assumption of the overall heat flux during hot catalyst-propellant contact in order to provide a gross estimate of heating time is 15 BTU/ 100 in.^{2} sec. Initial catalyst temperature was assumed to be 1000°F. Figure 28 shows that the propellant would ignite 0.333 second after contact (using a surface ignition temperature of 500°F).

(U) Table XVIII shows ignition times, heat required and heat available from various pyrotechnic and pyrogen charges to affect ignition at a point design with chamber pressure of 600 psia and chamber volume-to-propellant surface ratio of 4 to 1.

(c)   Heat Transfer Rate (U)

(U) After it was determined what heat sources and sinks were available, the time rate of change of the

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TABLE XVIII - IGNITION SYSTEM RESPONSE COMPARISON (U)

	Pyrotechnic (Smokeless Powder)	Pyrogen D-197	Pyrogen X*	Electrical 20 amps 24 VDC
1. Heat available in charge to raise chamber pressure to 600 psia at a V/S = 4 (BTU)	140	70	---	---
2. Heat required to heat 100 in.^{2} of catalyst bed at 500°F (BTU)	32	32	32	32
3. Heat required to ignite propellant** (function of heat flux) (BTU)	1.5	13.76	5.86	5
4. Heat flux to the propellant** (BTU/100 in.^{2} sec)	50	5.5	13	15
5. Time to ignite the propellant (sec)	.03	2.5	.45	51.***

*   Propellant with a gas temperature of 5320°F

**   Figure 28

*** Based on a 1000°F catalyst bed contacting propellant, time to heat catalyst bed at 500°F was 51 seconds and 0.333 second for the bed to ignite the propellant by conduction.

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propellant and catalyst bed was determined. The temperature-time history of a component was calculated by transient techniques. The time it takes to "heat" a body is a function of its thermal diffusivity characteristic length, exposed surface area and the driving force, the product of the overall heat transfer coefficient (thermal resistance) and the source to sink temperatures (thermal potential).

(U) Calculations of heat flux to the propellant were made over likely ranges of chamber pressure, ignition gas temperature, propellant surface ignition temperature, and transport properties of the ignition gases. The results of these calculations are shown on Figure 29 for 100 inches^2 of propellant surface area. Knowing the heat flux for an assumed set of pyrotechnic or pyrogen parameters from Figure 29, it is possible to predict time to surface ignition by entering Figure 28.

(U) The catalyst bed temperature rise versus exposure time to chamber gases is shown in Figure 30. The math model from which Figure 30 was derived assumes the external temperature difference is predominant, caused by a large internal to external heat conductance ratio (i.e. thermal conductivity divided by the product of the heat transfer coefficient and characteristic length).

(U) The heat transfer coefficient used in this study makes use of data describing heat transfer of an injected gas into a closed container, Reference (8).
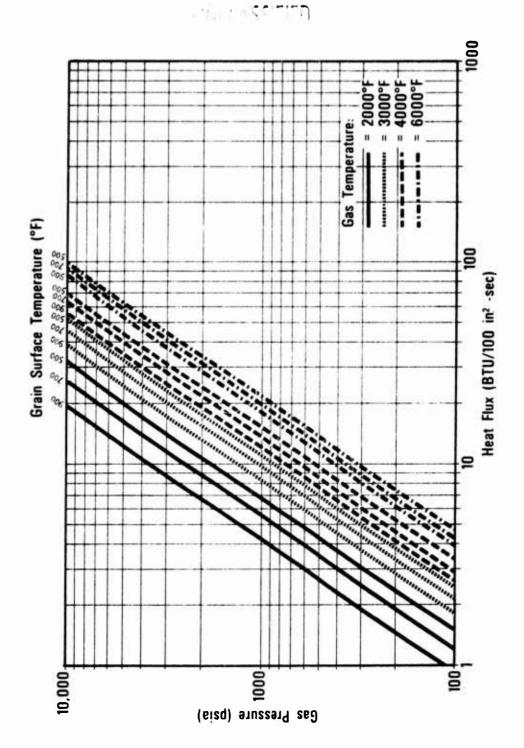
Figure 29 -   Chamber Gas Pressure vs Heat Flux for
Various Gas and Grain Surface Temperature (U)
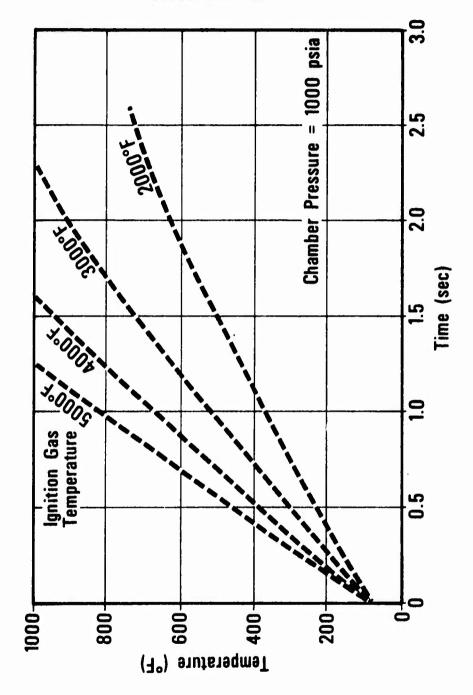
Figure   30 -   Catalyst Bed Temperature vs Time (U)

The results of Reference (8) show that the heat trans-
fer coefficients are two times higher than those re-
ported during the first two to four seconds of chamber
filling, then drop   to near those predicted by free
convection theory, indicating a decay of the initial in-
jection momentum to a flow pattern driven by a free con-
vection mechanism.

(U) Increasing the film coefficient by a factor
of two reduces the time to reach $500^{\circ}F$ with a $2000^{\circ}F$
gas source from 1. 5 seconds (see Figure 30) to 0. 76
second.

(U) Chamber pressure has a significant effect on
increasing the heat transfer coefficient and reducing
heating time. The heat transfer coefficient is propor-
tional to pressure to the 0. 667 power. Decreasing the
pressure a factor of two increases heating time by 59
percent.

(2)   Response Time (U)

(U) Delay time is defined as the time from ignition cir-
cuit closure until start chamber pressure rises.

(U) The pyrotechnic and pyrogen ignition designs   are
both initiated by electrical initiators (squibs); therefore, their
delay times are approximately equivalent to the initiator
functioning time of 0. 02 second.

(U) Delay time for the electrical ignition design   is
longer because no chamber pressurization occurs until the
propellant grain surface reaches ignition temperature via heat
transfer from the electrically heated catalyst bed

(approximately 51. 3 seconds).

(U) The rise time is defined as the time from start
of chamber pressurization to when chamber pressure reaches
ninety percent of the predetermined equilibrium pressure.

(U) The pyrotechnic system has the shortest rise
time because it uses the ignition mix to attain near equili-
brium chamber pressure; burning times range from 0. 010
to 0. 050 seconds.

(U) The mass flow rate from the pyrogen pressurizes
the gas generator chamber and defines the rise time of the
gas generator and can be varied by pyrogen design.   The
rise times may vary from 0. 5 second to 1. 6 seconds de-
pending on the range of ignition parameters expected to be
run.

(U) The rise time for electrical ignition designs is
dependent solely on the propellant grain for chamber gas
generation.   Figure 31 shows the rise time to be 0. 52
second to achieve 600 psia at a V/S ratio of 4.

(3)   Summary (U)

(U) Analyses of energies required to ignite and sustain
the R-500 propellant provided data for comparing the three
ignition techniques from a weight and volume standpoint.
Historical data, to date, on possible catalyst contamination
was reviewed for comparison.

(U) Table XIX is a summary of the ignition system
analysis.

(U) Considering the performance of the three systems,
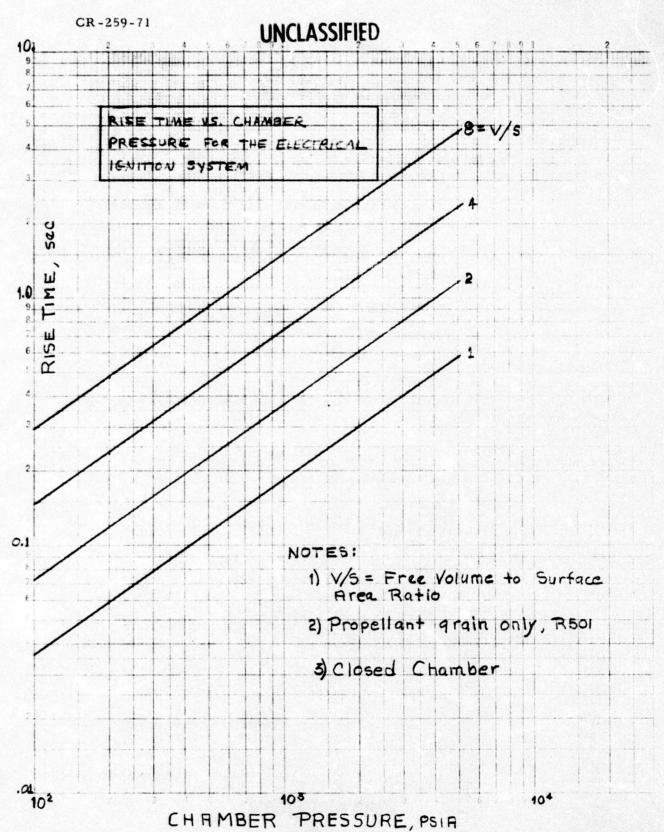
Figure 31 -   Rise Time vs Chamber Pressure for the Electrical
Ignition System (U)

Table XIX - Solid Demand Gas Generator Ignition Analysis Summary (U)

CHARACTERISTIC	PYROTECHNIC	PYROGEN	ELECTRIC
ENVELOPE			
WEIGHT	0.5 LBM	0.5 LBM	0.1 TO 1.0 LBM (PLUS 1.0 LBM)
VOLUME	+0.1 IN. GRAIN LENGTH	+5 CU. IN.	NONE (PLUS UNKNOWN)
PERFORMANCE			
DELAY TIME	0.02 SEC	0.02 SEC	17.0 SEC
RISE TIME (V/S=4,Pc=600)	0.01 TO 0.05 SEC	0.5 TO 1.6 SEC	0.5 SEC
CONTAMINATION	NO PROBLEM	MINIMUM	NONE
DESIGN CONSIDERATIONS			
POWER REQUIREMENTS	5 AMP/10 MSEC	5 AMP/10 MSEC	30 AMP/24 VDC FOR 17 SEC
MAINTENANCE	NONE	NONE	NONE
EASE OF FABRICATION	STATE-OF-ART (2)	STATE-OF-ART (1)	NEW (10)
COMPATIBILITY	NO FORESEEABLE PROBLEM	NO FORESEEABLE PROBLEM	NO FORESEEABLE PROBLEM
COST	LOW	MEDIUM	HIGH-MEDIUM
RELIABILITY	HIGH	HIGH	PROBABLE HIGH

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the electrical system was considered inferior due to its excessive delay time. In addition to the excessive delay time, the electrical power requirements (especially if the delay time is reduced) are high and the additional weight considerable.

(U) The differences between the pyrotechnic and the pyrogen ignition methods are slight. Due to the limited development of the electrical igniter system and the limited scope of this program, it was recommended that the pyrogen and pyrotechnic methods of ignition be selected for further evaluation. Complete details of the ignition system analysis are presented in the reference report (7).

d. Subscale Tests and Ignition System Selection (U)

(U) This portion of the ignition system development effort was to perform static tests which were to further evaluate the pyrogen and pyrotechnic ignition methods in the three-inch diameter test vehicle and select one ignition technique for further development in the twelve-inch diameter demand gas generator.

(1) Objective (U)

(U) The objectives of this task were to evaluate the pyrotechnic and pyrogen ignition systems and gather sufficient data to permit comparison of the two systems. Specifically, the detailed objectives were:

Pyrotechnic Igniter

- Compare M-7 propellant and smokeless powder and select one to use as the initiator for the pyrotechnic igniter.

- Determine the performance characteristics of the pyrotechnic initiator with an inert gas generator grain.

- Determine the ignition capability of the pyrotechnic igniter at high, low, and intermediate gas generator operating pressures.

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Pyrogen Igniter

- Determine the performance characteristics of the pyrogen igniter with an inert gas generator propellant grain.

- Determine the ignition capability of the pyrogen igniter at high, intermediate, and low gas generator operating pressures.

(2)   Tests (U)

(U) A total of thirty-five ignition tests was run in the three-inch diameter generator, seventeen of which were used to ignite overlay or main grain propellant.

(U) The test effort consisted of two series designated "A" for the pyrotechnic system and "B" for the pyrogen system. The three-inch diameter generator assemblies were tested at a $70^{o}F$ conditioning temperature. The K_n was adjusted to permit testing at high, intermediate, and low equilibrium pressure levels.

(U) A summary of the actual tests and the tests planned is presented in Figure 32.

(U) The three-inch gas generator assemblies included instrumentation to measure flame temperature, pressure, catalyst position and burn time. Instrumentation was as follows:

- Flame temperature: Type K thermocouples mounted upstream of the exhaust manifold

- Pressure: Two redundant 0 - 2000 psig pressure transducers mounted in the top plate of the motor case

- Catalyst position: A potentiometer provided an output proportional to movement of the catalyst control wheel

IGNITER DEVELOPMENT TEST PLAN
(TASK 2.4.C - EXPERIMENTAL TESTS)

Test Series B - Pyrogen Ignition

Inert Grain Tests
Vary Burn Time
Scheduled - 9
To Date - 8

Live Grain Tests
Scheduled - 5 at d_t = 0.070
-5 at d_t = 0.101
To Date - 4

Test Series A - Pyrotechnic Ignition

Smokeless Powder
Vary Charge Weight
Scheduled - 6 (Inert)
To Date - 5

M-7 Grains
Vary Length and Nozzle
Scheduled - 6 (Inert)
To Date - 12

Select Pyrotechnic Ignition System
M-7 Grain Selected

Test W/W:700 G/L and Inert Grain
Scheduled - 4
To Date - 3

Ten Generator Tests
Scheduled - 5 at d_t = 0.070
-5 at d_t = 0.101
To Date - 10

Final Evaluation - Select Ignition System for 12- Inch Generator Tests

Figure 32 - Igniter Development Test Plan (U)

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• Burn time: A timing reference provided
the time base on the oscillograph trace.

(U) Data from the above instrumentation was amplified
and fed to a multi-channel recorded CEC oscillograph
which provided a trace of each parameter on a permanent
record.

(3) Design Description (U)

(U) Pertinent design data on the pyrotechnic and pyro-
gen ignition systems are given in Section IV. 3 and more de-
tailed descriptions are given in Reference (9).

(4) Test Results (U)

(U) The following paragraphs describe test results of
the pyrotechnic and pyrogen ignition systems. Test load
sheets and oscillographs for the three-inch diameter gas
generator tests are given in Exhibit A (Volume II) of Refer-
ence (9).

(a) Test Series A - Pyrotechnic (U)

(U) Seventeen tests were fired using the pyro-
technic initiator with an inert overlay and inert grain
in three-inch diameter hardware to establish a relation-
ship between initiator charge size and chamber pres-
sure for smokeless powder and M-7 propellant charges.

(U) Table XX is a summary of the smokeless
powder initiator test results. The results show erratic
pressures caused by inefficient burning of the smoke-
less powder resulting from varying degrees of powder
ignition before powder combustion products were

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TABLE XX - PYROTECHNIC INITIATOR TEST SUMMARY (smokeless powder) (U)

Test No.	Smokeless Powder		Pressure-psia		Nozzle dia., in.		Remarks
	Type	Weight, Grams	Igniter	Chamber	Igniter	Chamber	
138	Hivel No. 2	2.0	179	42	0.300	0.070	Low pressures
139	Hivel No. 2	4.0	1162	71	0.250	0.070	Overpressurized igniter port
140	Hivel No. 2	3.0	280	277	0.300	0.070	Apparent ignition of residual powder in chamber (from previous test) 0.8 sec after ignition.
141	Hivel No. 2	3.5	698	39	0.300	0.070	Low pressures
142	Hivel No. 2	4.0	271	268	0.300	0.070	Same results as Test 140.

NOTES: Single initiator used on each test

exhausted into the chamber. Smokeless powder testing was stopped after five tests because of poor test results.

(U) Table XXI is a summary of M-7 propellant charge initiator tests. The initiator design was frozen after these tests and three additional tests were run with the frozen design. These tests are summarized in Table XXII. A typical pressure-time curve of these tests is given in Figure 33.

(U) Following the design of the initiator, ten tests were run using M-700 propellant overlay cast on a R-500 propellant grain. A summary of these tests is given in Table XXIII.

(U) Chamber pressure fluctuations during overlay and main propellant burning occurred during these tests and geometrical changes were made on the overlay based on acquired ballistic information. Overlay geometry was also changed to provide more heating time to the catalyst bed. Figures 34 and 35 show typical chamber pressures experienced during this test series.

(b)   Test Series B - Pyrogen (U)

(U) A total of five pyrogen igniter tests was run. The tests are summarized on Table XXIV. Except for a nozzle blockage on the last test, No. 261, pyrogen pressures and burn times were as predicted, and ignition of the pyrogen was achieved in all cases. In none of the tests did the pyrogen ignite the R-500 grain. Figure 36

Test No.	Number Igniters	Grain[1]	Wt., gms	Booster	Igniter P max psi	Burn time, sec	Nozzle, inch	Chamber[2] Pressure, psia P max	P min	P steady	Nozzle, inch	Remarks
136	2	0.875	3.2	---	638	0.115	0.108	38	---	---	0.070	Long ignition delay
137	1	1.125	2.1	.2 gm Hivel #2	2132	---	0.108	---	---	---	0.070	Overpressurized igniter blowout port at 2132 psi
157	1	1.375	2.3	.25 gm 3 Fg BP[3]	758	0.035	0.136	108	88	100	0.070	
158	1	1.375	2.5	.25 gm 3 Fg BP[3]	2680	0.030	0.120	212	---	---	0.070	
159	1	1.375	2.6	.25 gm 3 Fg BP[3]	1336	0.040	0.120	197	---	155	0.070	
174	2	1.35	---	.3 gm 3 Fg BP[3]	1640	0.045	0.120	393	---	393	0.070	
175	2	1.375	5.1	.3 gm 3 Fg BP[3]	1916	0.035	0.121	474	---	---	0.070	
181	2	1.375	5.1	.3 gm 3 Fg BP[3]	1672	0.055	0.121	---	---	---	---	Blowout port in chamber open, providing a 1/2" diameter orifice.
182	2	1.45	5.5	.3 gm 3 Fg BP[3]	1533	0.050	0.121	---	---	---	---	Same as above
183	2	1.50	5.2	.3 gm 3 Fg BP[3]	1775	0.045	0.121	---	---	---	---	Same as above
184	2	1.50	5.6	.3 gm 3 Fg BP[3]	2030	0.037	0.121	---	---	---	---	Same as above
185	2	1.65	6.15	.3 gm 3 Fg BP[3]	2692	0.055	0.121	---	---	---	---	Same as above

(1) M-7 propellant 0.135 ID x 0.320 OD (2) Inert propellant grain in gas generator chamber
(3) Black powder (BP) (4) Gas generator pressures disregarded tests 181 thru 185 since chamber blowout port was open.

TABLE XXI - PYROTECHNIC INITIATOR TEST SUMMARY (M-7 propellant)(U)

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Test No.	Igniter Maximum Pressure, psia	Gas Generator Pressure, psia				Time (sec) to Reach		Burn Time, (sec)		Remarks
		P_{ign}	P_{min} (saddle)	P_{max}	P_{ss}	P_{min} (saddle)	P_{ss}	P_{ss}	Total	
186	1566	608	330	1504	---	0.245	---	---	5.13	Irregular burning Surface trimmed with knife.
198	1922	705	420	635	605	0.250	1.97	3.32	5.29	Surface trimmed on lathe.
199	2480	670	445	600	571	0.350	1.84	4.23	6.08	Same as above

NOTES:

1. M-7 grain 1.6" long x 0.135" ID x 0.330" OD (Radford M-7).

2. Two igniters used in each test.

3. M-7 weight 6.1 grams (total) with 0.3 grams 3 Fg booster charge each igniter.

4. M-700 propellant overlay 0.380" thick covering entire surface of R-500 grain.

5. All tests conducted with catalyst bed in maximum up position.

6. All tests conducted with a 0.070 inch diameter nozzle in the generator.
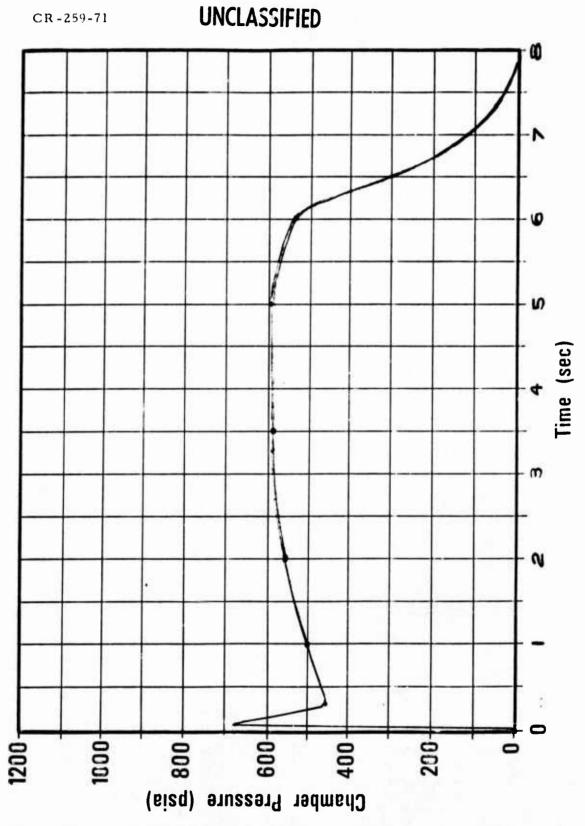
* Steady state pressure

TABLE XXII- FROZEN PYROTECHNIC IGNITER TEST SUMMARY (U)

Figure 33 - Typical Pressure-Time Curve, Pyrotechnic Igniter (U)

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TABLE XXIII - PYROTECHNIC IGNITER TEST SUMMARY (U)
(M-7 igniter, M-700 overlay, R-500 grain)

Test No.	Pressures, psia, during ignition				Time, seconds during ignition			Overlay		Initial Catalyst Position	Kn		Chamber Pressure, psia R-500	Remarks
	Ignition	Saddle	Max	Steady State	To Saddle	To Steady State	Total Igniter Burn	Dia. In.	Thickness In.		R-500	M-700		
200	640	425	590	590	0.35	1.7	3.2	2.96	0.320	Full up	1784	1784	250	Catalyst put on overlay at overlay burn out.
209	660	404	420	400 (prior to bed down)	0.30	0.65	---	2.96	0.312	Full up	1784	1784	---	Generator overpressurized when catalyst put on grain at t=0.9 sec. Post-fire inspection showed catalyst burned through overlay.
248	372	155	230	210	0.28	1.5	3.5	1.7	0.350	Full up	1784	590	588	Sides of overlay inhibited. Catalyst put on overlay near burnout. Slow rise time (23 sec) to chamber pressure.
249	419	202	544	500	0.50	2.0	3.5	1.75	0.350	Full down	1784	605	525	Sides of overlay not inhibited.
250	434	149	318	265	0.80	3.0	4.0	2.25	0.30	Full down	1784	1033	600	Sides of overlay not inhibited.
251	443	246	1613	---	0.40	---	2.5	2.50	0.30	Full down	1784	1275	460	Chamber pressure humped to 1600 psi at t=2 sec.
253	500	268	380	---	0.50	---	3.5	2.25	0.275	Full down	1784	1033	800	Sides of overlay not inhibited. Chamber pressure slow rise (24 sec) to steady state pressure.
254	496	52	228	100	1.35	3.3	6.5	2.25	0.225	Full down	857	496	175	Sides of overlay not inhibited.
255	550	118	250	250	1.15	3.85	7.8	2.25	0.220	Full down	2202	1275	650	Chamber pressure (R-500) slow rise (20 sec) to chamber pressure.
256	583	268	1016	---	0.40	---	2.5	2.25	-.275	Raised 1/4 in.	1784	1033	400	Sides of overlay not inhibited. Bed dropped t=1.4 sec. Overlay burnout at 1000 psi.

NOTES: Two igniters used;   M-7 grain 0.330" OD x 0.135" ID x 1.6" long;   Total weight M-7 = 6.0 grams

Booster charge 0.3 gram E Fg BP each igniter;   Holex 1196A squib initiator

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PYROTECHNIC IGNITION - TEST 254
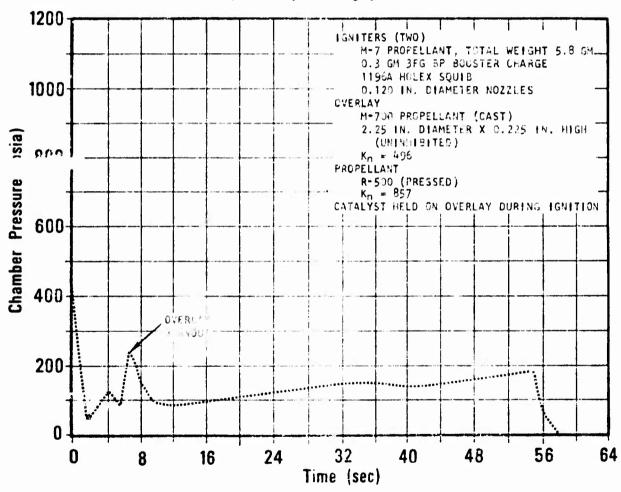### (Low operating pressure)

Figure 34   —   Pressure-Time Curve for Pyrotechnic Test 254 (U)

PYROTECHNIC IGNITION - TEST 255
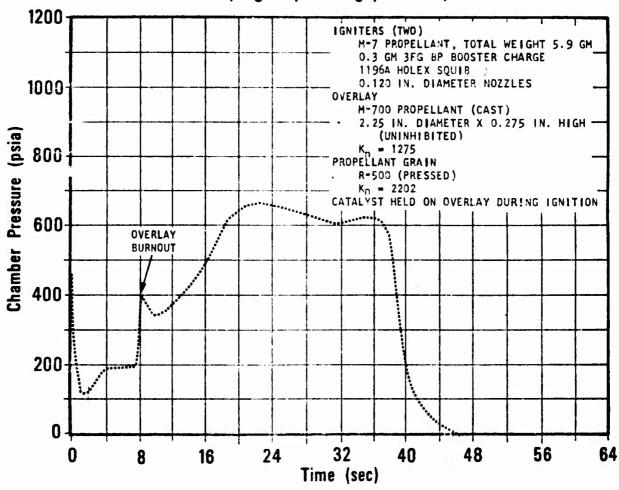### (High operating pressure)

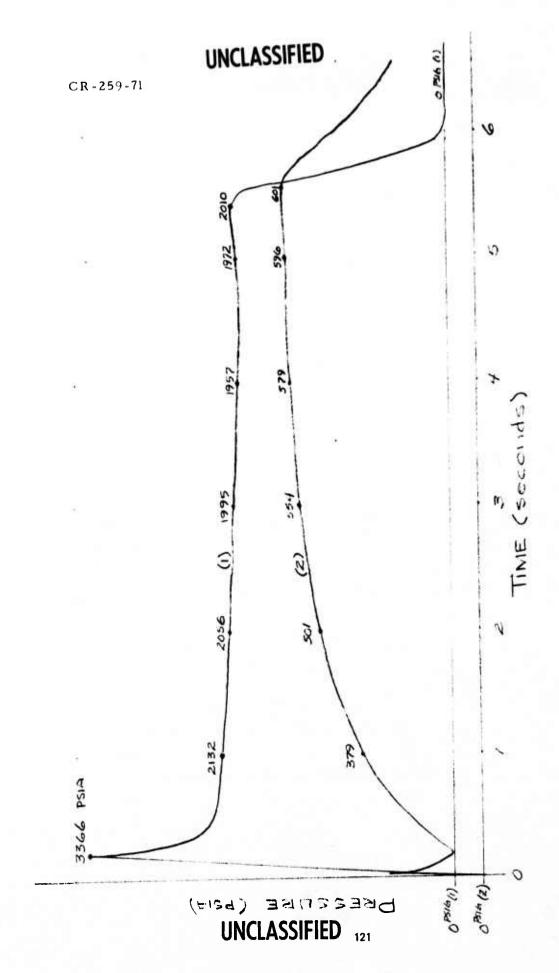Figure 35 - Pressure-Time Curve for Pyrotechnic Test 255 (U)

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Test No.	Grain Propellant	Grain Length, Inch	Grain Dia. Inch	Ignition Booster	Nozzle Dia. in.	Psia Max.	Psia Avg.	Time-sec Rise (2)	Time-sec Total	Pyrotechnic Booster (1)	Gas Generator Chamber Propellant	Nozzle Dia. in.	Catalyst Position	Pressure psia (3)
213	D-198	1.5	1.5	.5 gm 3 Fg BP	.040	1747	1664	10.48	58.58	No	Inert	.070	Down	414
214	D-198	1.6	1.5	.7 gm 3 Fg BP	.040	1852	1688	1.106	5.32	No	R-500	.070	Down	468
215	D-198	1.6	1.5	.7 gm 3 Fg BP	.040	2366	2146	0.15	5.29	Yes	R-500	.070	Down	515
251	D-198	1.6	1.5	.7 gm 3 Fg BP	.046	--	--	--	--	Yes	R-500	.070	Down	--
201	D-198	1.6	1.5	.9 gm 3 Fg BP	.052	822	--	0.69	9.17	Yes	R-500	.070	Down	--

Remarks (213): Catalyst bed filled with carbon deposit from pyrogen. Generator pressure 549 psi at pyrogen burnout.

Remarks (214): Good pyrogen pressure. Chamber pressure ramped to 601 psia. R-500 did not ignite.

Remarks (215): Catalyst bed moved off R-500 grain at ignition. Returned to grain at t=.4 sec. Good pyrogen pressure. Chamber pressure 504 psia at R-500 did not ignite.

Remarks (251): Catalyst bed moved off R-500 grain at ignition. Returned to grain at t=.75 sec. Pyrogen did not ignite initially. Pyrogen ignited 30 sec after instrumentation turned off. Obtained generator pressure of 580 psi at burnout.

Remarks (201): Catalyst bed raised up at ignition. Returned to grain 1.5 sec after ignition. Chamber nozzle apparently clogged as chamber pressure ramped to 1010 psi and nozzle cleared at t=3.4 sec. Generator pressure 281 psi at burnout.

Notes:

(1) Pyrotechnic booster consisted of single igniter with 3.0 grams M-7 propellant. 0.330" OD x 0.135" ID x 1.6" lgt.

(2) Rise time: from t=0 to t=90% Pavg in pyrogen.

(3) Average gas generator chamber pressure.

TABLE XXIV - PYROGEN IGNITER TEST SUMMARY (U)

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FIGURE 36 - Pressure - Time Curve for Pyrogen Test 215 (u)

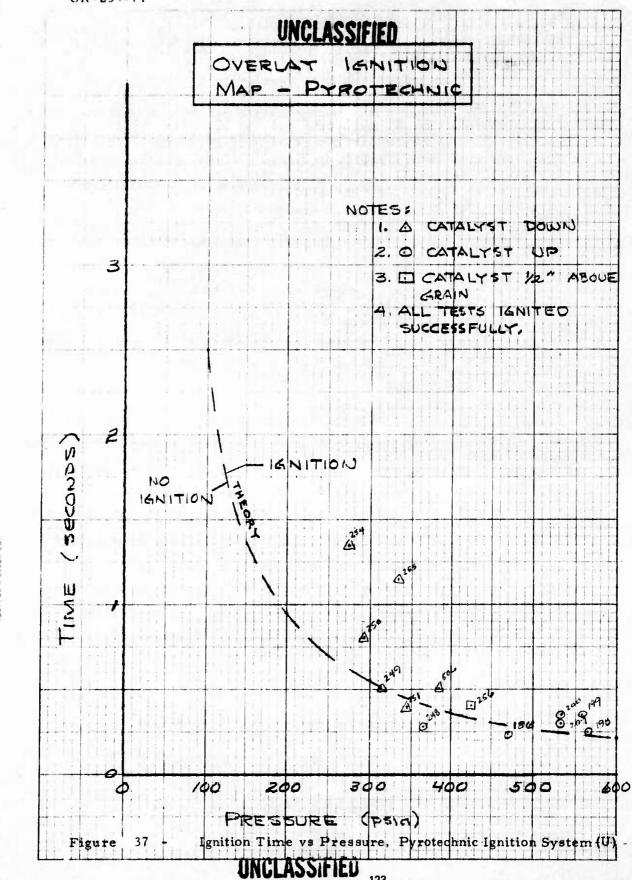**UNCLASSIFIED**

shows typical pressures traces for the pyrogen and gas generator chambers.

(5)   Test Analysis (U)

(a)   Test Series A - Pyrotechnic

(U) Gas generator pressure perturbations during overlay propellant burning and during R-500 propellant burning resulted from the two different stimuli.

(U) Examination of ballistic data during overlay burning showed that the M-700 overlay propellant was catalytic. It was determined that the apparent erratic Pc - K_n data for M-700 in catalysis was in fact a family of Pc - K_n curves which was a function of catalyst bed temperature or net instantaneous surface heat flux.

(U) Pressure perturbations during R-500 propellant burning was attributed to insufficient heating of the catalyst bed and nonsteady state thermal conditions between the catalyst bed and propellant surface.

(U) Overlay propellant ignition was accomplished between 0.23 and 1.35 seconds depending on the catalyst bed-overlay configuration and chamber pressure which varied from 200 to 570 psia.

(U) Figure 37 is a plot of overlay ignition time versus chamber pressure. The thirteen ignition points are plotted along with a theoretical curve taken from a cross plot of Figures III-1 and III-9 in Reference (7).

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Figure 37 — Ignition Time vs Pressure, Pyrotechnic Ignition System (U)

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(b)   Test Series B - Pyrogen (U)

(U) The unsuccessful pyrogen test ignitions were caused by low heat flux at the propellant surface. All tests were run with the catalyst bed on the propellant which promotes stagnant gas conditions at the catalyst bed/propellant interface.

(U) Figure 38,   a cross plot of Figures III-1 and III-9 from Reference (7), shows   ignition time versus propellant autoignition temperature as a function of chamber pressure.   Also plotted on Figure 38   are the three pressure-time conditions of Tests 214, 215, and 261--all of which had no ignition of the R-500 grain.

(U) The five-second autoignition temperature of R-500 propellant is $675^{\circ}F$.   Test 261 ran eleven seconds at an average pressure of 520 psia.   When plotted on Figure 38,   the surface ignition temperature is estimated to be $663^{\circ}F$ which is below the R-500 autoignition temperature.   (Had Test 261 maintained gas generator chamber pressure longer, the intersection of the 520 psia curve and the $675^{\circ}F$ autoignition temperature shows the surface would have ignited at twelve seconds.)   The other two tests showed autoignition temperatures of $524^{\circ}F$ and $568^{\circ}F$.

(6)   Conclusions (U)

(a)   Pyrogen (U)

● (U) Failure to cause grain ignition within ten

Figure 38 - Ignition Time vs Surface Ignition Temperature (U)

seconds when using the pyrogen ignition design
was a result of low heat flux at the propellant-
catalyst interface.

- (U) Heat flux at the propellant surface was
  reduced because of gas stagnation caused by
  the catalyst bed in its down position.

- (U) Analyses show that ignition of the propellant
  surface within ten seconds is marginal even
  when the propellant surface is not shielded by
  the catalyst bed.

- (U) Three-inch diameter test results have veri-
  fied the long ignition times indicated by analytical
  methods. These results can be shown to be scal-
  able for the twelve-inch vehicle via dimensional
  analysis. Thus, grain ignition from a pyrogen
  cannot be achieved within a reasonably short
  period of time with the current test hardware
  unless a more energetic pyrogen propellant or
  high chamber pressures are incorporated.

(b) Pyrotechnic (U)

- (U) The propellant overlay can be reliably ignited
  by conventional pyrotechnic methods when the
  catalyst is either on or off the overlay surface,
  as verified by 13, three-inch diameter tests.

- (U) Overlay propellant ignition was accomplished
  between 0. 23 and 0. 36 seconds when the catalyst
  was withdrawn 2. 3 inches from the propellant

surface.   These times were demonstrated in
six tests over a pressure range from 360 to
570 psia.   Overlay propellant ignition was accom-
plished between 0. 40 and 1. 35 seconds when the
catalyst was in contact with the overlay surface.
These times were demonstrated in six tests over
a pressure range from 200 to 350 psia.   Three-
inch diameter generator test results show that
propellant overlay ignition is accomplished in a
shorter period of time, given the same pressure-
temperature-time environment, if the catalyst is
withdrawn from the overlay surface.

- (U) Chamber pressure perturbations encountered
  during M-700 overlay burning is attributed to the
  erratic catalysis of the burning rate which occurs
  when nonsteady state heat transfer exists between
  the catalyst bed and the overlay surface.

- (U) Catalysis of overlay burning rate must either
  be controllable (using a bistable controller) or
  eliminated.

- (U) Catalyst heating can be most rapidly accom-
  plished if the catalyst is positioned above the pro-
  pellant combustion zone.

- (U) Transition from overlay burning to main
  grain burning has been demonstrated in the three-
  inch diameter test series.   Improvement in the
  reproducibility and smoothness of this transition
  is needed.

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(7)   Recommendations (U)

- (U) It was recommended that the pyrotechnic ignition technique be selected for further development in the twelve-inch diameter vehicle.

- (U) It was recommended that further three-inch diameter tests be conducted to eliminate pressure perturbations. Improvements can be accomplished by tests 1) in which several overlay candidate propellants are incorporated that have ballistic properties more compatible with those of the main grain, and 2) that show the effects of overlay configuration on reducing overlay catalysis and heating time of the catalyst bed.

- (U) It was recommended that the test plan for further three-inch diameter and twelve-inch diameter tests be made.

e.   Ignition Analyses and Tests (U)

(1)   Analyses and Test Results (U)

(U) Analyses on the thermal response of the catalyst bed and R-500 propellant during burning of D-198 overlay propellant. D-198 propellant was selected as an overlay because it was noncatalytic. Analyses showed that varying the overlay geometry could help to raise the catalyst bed temperature during overlay burning by fifty percent.

(U) Eleven,three-inch diameter ignition tests were run varying the overlay/catalyst bed configuration. The trend of these tests match the analysis trend but it was apparent that the absolute temperature levels of components were significantly

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different than the predicted temperatures.

(U) Similar results occurred on five, twelve-inch diameter tests.

(2)   Conclusions (U)

(U) It was known that the overlay designs in each test contained at least three times as much thermal energy as that required to adequately heat the b and R-500 propellant.

(U) It was also concluded that there was a significant difference in catalyst bed and R-500 propellant radial temperature profiles with the various overlay configurations used.

(U) It was concluded that to get the required heat to the catalyst bed screen was at most a tailoring problem and slight tailoring modifications to date had yielded little positive results.

(3)   Recommendations (U)

(U) It was recommended that a more thorough thermal analysis be made and that the overlay configuration of the remaining three, twelve-inch diameter tests be sized as a result of the analysis of each previous test.

f.   Analyses and Tests of the Final Twelve-Inch Diameter Generator (U)

(1)   Analyses (U)

(U) The apparent difficulty of matching theoretical thermal responses of the catalyst bed and the actual responses was clouded by facts that it was not known at exactly what

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thermal conditions should exist within the bed and R-500
to affect steady state catalysis, that there was suspicion
that the activity of the catalyst beds were variable, that
there were large zones of thick melt layers on the R-500
propellant surface prior to overlay burnout, and that the
general thermal prediction model did not incorporate a re-
quired variable.

(U) Dr. E. R. G. Eckert, Director of the Heat and
Mass Flow Laboratory at the University of Minnesota was
contacted to review the math model. Dr. Eckert agreed with
the approach and math model. It was concluded that the
heat transfer film coefficient through the screen was proba-
bly the item that could be concentrated on. Professor
Eckert agreed with the use of Reynolds' analogy for determin-
ing the heat transfer coefficient on the catalyst screen.
While the fluid flow-friction data on the Proctor and Gamble
report, Reference (10), which was being used, showed good
results between test data and analytical predictions, Eckert
suggested that data from Reference (11) could be used.

(U) As a result of this consultation, Kays and London
data were examined and incorporated as the method for
determining the heat transfer coefficient of the catalyst bed.
Kays and London data gave heat transfer coefficients forty
percent lower than those calculated via Reynolds' analogy
from Reference (10) at low values of overlay gas leakage rates
around the catalyst bed. At high overlay gas leakage rates,
the Kays and London data were lower than that from Reference
(10) by a factor of four.

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(2)   Test Results and Conclusions (U)

(a)   Test 12 (U)

(U) Test 12 employed two fixes to provide for sufficient heating and a more uniform radial temperature distribution on the catalyst bed. First, the overlay propellant web was increased fifty percent to provide additional heating time and more mass flow per unit area to the outer radial portions of the catalyst bed. Secondly, the overlay standoff strips were ballistically designed to hold the catalyst bed off the overlay until the overlay web was 90 to 95 percent consumed. The design configuration was roughly similar to those used in Tests 10 and 11 except that the web and mass of the overlay was increased fifty percent.

(U) Test 12 experienced a successful overlay ignition. Immediately after overlay burnout, the chamber pressure increased, indicating augmented catalysis of R-500. The chamber pressure then dropped below the predicted level and the pressure perturbations occurred.

(U) Test 12 was a failure from an ignition standpoint; however, it did provide data which 1) indicated that one of the parameters affecting heat transfer was insufficiently accounted for, and 2) revealed the cause of poor ignitions.

(U) The initial augmented burning rate of the R-500 propellant was caused by the superheated catalyst bed screen that was facing the propellant. Thermal

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inertia of the bed was insufficient to sustain a re-
generation of heat within the bed from catalysis.

(U) A heat and mass transfer analysis was per-
formed on the gas generator chamber. The result
of this analysis was that the catalyst bed was unsuf-
ficiently heated; the actual heat input into the catalyst
bed was one-half of that calculated during overlay
burning. This was determined by calculating the
amount of energy available in the overlay and sub-
tracting the amount of energy exiting the gas generator
nozzles.

(U) Investigation into the cause of the reduced heat
transfer to the catalyst bed revealed that excessive
amounts of overlay combustion products were leaking
around the outer diameter of the catalyst bed. This
was caused by two things: 1) a significant diametral
clearance between the catalyst bed outer diameter and
the inner diameter of the case insulation, and 2), the
catalyst bed which was used in Test 12 had the highest
resistance to flow of any beds tested at that time. This
excessive leakage around the bed was calculated to reduce
the heat transferred to the bed by a factor of 2.7.

(U) The reduction in overlay combustion products
flowing through the catalyst bed had less effect on re-
ducing the temperature of the first screen than it did on
the second and third screens. The first screen essentially

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experienced gas at combustion temperature flowing
through it and across its forward surface. The
second and third screens experienced the combustion
products at lower temperatures because as the gas
flows through the bed, it loses heat to the bed.

(U) To insure that the overlay combustion pro-
ducts would travel through the catalyst bed, it was
decided to use a full overlay and set the catalyst bed
down on the overlay. This would, in effect, enable each
square inch of catalyst bed to "capture" that portion of
overlay combustion products immediately under it.
The resistance to flow rate through the catalyst bed
would be lower than the radial path between the bed and
propellant surface to the bed O. D. /case insulation I. D.
clearance.

(U) Table XXV shows pretest (Test 12) catalyst
bed temperature predictions and post-test calculations
using the conservation of energy calculations with the
test data input and predictions for Test 13.

(b) Test 13 (U)

(U) Test 13 employed a full overlay. The base
propellant K_n value was extrapolated from nonsteady
state catalytic rates from previous tests.

(U) At ignition, the blowout port on the pyrotechnic
initiator ruptured. It was later determined that the
initiation was improperly assembled causing over-
pressure in the initiator chamber.

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TABLE XXV

CATALYST BED TEMPERATURE ESTIMATIONS (U)

		Screen 1 (°F)	Screen 2 (°F)	Screen 3 (°F)
1.	Pre-test 12 (Cylindrical Theory)	1520	1335	1150
2.	Post-test 12 (Conservation of Energy)	910	710	510
3.	Prediction for Test 13	1470	1380	1290

(U) There was no ignition in the main chamber due to a low pressure-time integral.

(c)   Test 14 (U)

(U) Test 14 had the same configuration as Test 13 except the initiator was properly assembled. Extrapolation of the base grain K_n from Test 13 yielded a chamber pressure after overlay burnout that was too high, rupturing the chamber blowout port.

(U) The catalyst was probably heated to its critical value negating the nonsteady state K_n data. Augmentation of catalysis due to the hot catalyst bed was encouraging for ignition progress.

(U) It was decided to adjust K_n value to comply with the latest ballistic findings and continue with the apparently successful overlay design.

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(d)   Test 15 (U)

(U) The initiator and overlay performance of Test 15 yielded a successful ignition within three seconds.   The test duration was 202 seconds.

(e)   Tests 16 through 24 - System Tests (U)

(U) All subsequent twelve-inch diameter gas generator tests ignited successfully except for Test 22.

(U) During Test 22, the catalyst bed locked in position during overlay burning; the overlay surface burned away from the catalyst bed resulting in a catalyst bed heating situation similar to the partial overlay design (i. e. leakage around the catalyst bed occurred).

g.   Conclusions (U)

(U) The ignition tests and system tests showed that there was always enough heat available in the overlay to heat the catalyst bed propellant to its critical value.

(U) Difficulty in   predicting catalyst bed thermal response was eliminated when it was established that the leakage around the bed was higher than that originally calculated.

(U) Steady state catalysis of the R-500 propellant is possible only after the whole catalyst bed has been brought to its critical value.

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(U) Inadequately heated catalyst beds yield erratic catalysis resulting in significant chamber excursions. The mechanism of regenerative heating of the catalyst bed during unsteady state catalysis is poor and unpredictable if the bed has not been brought to its critical thermal level.

(U) Steady state catalysis during bistable control is in reality a transient thermal condition that exists between the catalyst bed and R-500 propellant in which the periodic temperature profile under the regressing propellant surface and the periodic thermal response of the catalyst bed vary between acceptable, stable limits.

h. Summary (U)

  (1) Analytical Study (U)

    (a) Candidate systems - pyrotechnic, electrical, pyrogen

    (b) Parameters investigated - heat required, time required, weight and volume

    (c) Conclusions - Responses of electrical heating type systems were prohibitively long

    (d) Recommendations - Further evaluate the pyrotechnic and pyrogen ignition system schemes in three-inch diameter motors.

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(2) Ignition System Selection (U)

    (a)   Tests (U)

- Thirty-pyrotechnic system
- Five-pyrogen system

    (b)   Results (U)

- No motor ignition with pyrogen system at ignition design pressures

- All pyrotechnic tests sustained ignition

- Chamber pressure perturbations occurred ater ignitions.

    (c)   Conclusions (U)

- The pyrogen ignition system, as designed, required higher chamber pressures to ignite the base propellant successfully.

- Pressure perturbations occurring after ignition with the pyrotechnic system was the result of erratic catalytic action of the selected overlay propellant caused by non-steady state heat transfer conditions between the catalyst bed and the propellant surface.

    (d)   Recommendations (U)

- Select pyrotechnic system for further development.

- Additional three-inch and twelve-inch diameter tests be run to improve transition

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from overlay to base grain.

- Use a noncatalytic propellant for overlay.

(3)   Additional Ignition System Testing (U)

    (a)   Tests - Variable Overlay Geometries (U)

- Eleven, three-inch tests

- Five, twelve-inch tests, inert base grain

- Six, twelve-inch tests

    (b)   Results (U)

- Pressure perturbations, less than with catalytic overlay

    (c)   Conclusions (U)

- Ignition perturbations viewed as tailoring problem.

- Enough heat was available in overlay, but the rate of heat transfer was too low. Can be corrected by tailoring.

    (d)   Recommendations (U)

- Start detailed analytical thermal analyses of ignition sequence.

- Run the remaining four ignition tests using results of thermal anal, ...s. Analyses of each test would be input to design overlays of subsequent tests.

(4)   Final Stages of Ignition System Development (U)

(a)   Tests (U)

- Test 12 - increased overlay thickness and mass

  - No improvement in reducing pressure perturbations.

  - Heat and mass flow analyses showed bed was insufficiently heated and the catalyst bed lacked thermal inertia to sustain steady state catalysis.

  - This test was an ignition failure but conclusively provided data to make a significant change to the overlay.

- Test 13 - full overlay, base propellant K_n extrapolated from nonsteady state catalytic rates

  - Initiator improperly assembled causing initiator blowout port to rupture.

  - Failure to ignite overlay during brief chamber pressurization period was confirmed against the ignition system analysis report prediction.

- Test 14 - same configuration as Test 13, with properly assembled initiator.

  - Extrapolation of base grain K_n from Test 13 yielded too high chamber pressure; ruptured chamber blowout port.

  - The catalyst was probably heated to its critical value negating the nonsteady state K_n data; encouraging for ignition progress.

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- Test 15 - full overlay, adjusted K_n

    - Successful ignition with three seconds

    - Test duration was 202 seconds.

(5) Started Controller Tests (U)

  (a) Tests

    - Tests 16-22, only Test 22 failed to sustain a proper ignition.

  (b) Test 22

    - Catalyst bed did not follow overlay during overlay burning. Leakage around bed (found in detailed analysis) is significant; second and third screens were insufficiently heated.

(6) Ignition System Design (U)

  (a) Configuration

    - Initiator with full overlay of D-198 propellant, 0.3-inch web.

  (b) Evolved By

    - Finding a configuration that has a very high heat flux

  (c) Possible Improvement

    - Decrease the amount of mass in the overlay (excessive heat is available but not transferred to the catalyst bed).

    - Decrease leakage around the bed.

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8.   CONTROL SYSTEM DEVELOPMENT (U)

    <u>a</u>.   <u>Introduction</u> (U)

        (U) The function of the catalyst control mechanism (controller) is to maintain constant gas generator plenum pressure within a relative narrow bandwidth and under changing volume and mass flow rates.   The generator pressure fluctuates about a preset nominal pressure, i.e., 600 psia, according to the mass flow demand on the gas generator.   When a demand is placed on the generator, the pressure drops below the nominal pressure.   When a lower limit pressure, i.e., 597 psia, is reached, an electrical command signal is sent to the control system to move the catalyst onto the propellant surface.   As the pressure rises past the nominal and through an upper limit, i.e., 603 psia, an electrical signal is sent to the control system to move the catalyst away from the propellant surface.   The prime mover for the control system can be pneumatic, hydraulic, or electrical.   This type control system operation is classified bistable (bang-bang) operation versus a proportional operation, which would position the catalyst given distances away from the propellant grain surface depending on the gas mass flow requirements.

        (U) The objective of the control system development portion of the program was both long range and short range.

        (U) The short range program objectives were:

- To develop actuation test assemblies that would interface with the existing 12-inch diameter DGG test bed to prove its concept and function under simulated and warm gas firings.
- The unit was to accept three actuator systems.

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- Through bistable operation of the control system in the pulse duration control mode via pressure feed back commands, to maintain constant gas generator pressure within acceptable limits at different pressure and mass flow levels.

    (U) The long range program objectives were:

- Adaptability of control system to present and advanced DGG concepts.

- To gain sufficient knowledge to scale and incorporate the control system into full scale light weight components.

- To gain information on reliability factors, storage capability and power requirements of the assembly.

b. Approach (U)

(U) The catalyst control system development approach consisted of an analysis of potential controllers, the selection of the three most promising designs, the design fabrication and cold gas testing of two selected controllers and the warm gas testing of the best system.

(U) A literature search was made and a system analysis was conducted on hydraulic, pneumatic, and electrical methods for controlling the catalyst movement. An evaluation of the three systems based on the literature survey and gas generator system computer studies rated the warm gas pneumatic system the highest with the electrical and hydraulic system rated second and third, respectively.

(U) Computer analyses were conducted with the bistable control system. The studies as well as the cold and warm gas control and system tests showed that this mode of operation has the ability to maintain a constant gas generator pressure within

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a relatively narrow band width at different mass flows and pressure levels.

(U) The computer analysis also showed the effect of changing free volume in the gas generator chamber with respect to the propellant burning surface (v/s ratio) on the gas generator pressure and mass flow variations from nominal levels. The higher the v/s ratio, the less the amplitudes vary from nominal. The computer analysis showed the turbo pneumatic control system with it's relatively slow response rate to result in greater pressure variation amplitudes, whereas the electrical actuation method provided the least deviations from nominal over a range of v/s ratios from 3 to 20.

(U) Specifications were written; inquiries from industry solicited and evaluated; and recommendations made for the selection of three vendor proposals. Selections were made as follows:

- Turbo-pneumatic - Philco-Ford Astronautics Division
- Electrical - Photocircuits Corporation, PMI Division
- Hydraulic - Vickers, Inc.

In addition to the above vendor selections, NCI evaluated a pneumatic system with a reciprocating actuator which proved to have a better response time than the turbo pneumatic system.

(U) Only the hydraulic and electric actuators were subjected to cold gas tests. All warm gas tests were performed with the electric actuator.

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c. Requirements (U)

(U) In order to arrive at a set of requirements for the various control systems, the following ground rules were established:

- Performance requirements were established for the control system based on the present NCI 12-inch diameter gas generator.

- The control system was to operate in the bistable (bang-bang) mode in which the propellant mass flow is varied by PDM.

(U) Figure 39 is a functional schematic of the 12-inch diameter test demand gas generator. Based on the performance of the gas generator with a pneumatic piston bistable control system, a torque level requirement of 60 inch-pounds was established for the control system. Table XXVI is a summary of the 12-inch gas generator control system torque levels. As noted on the schematic, the travel distance of the catalyst bed was 0.35 inch and the retracting time required was 0.030 seconds.

(U) An important parameter to the control system is the retraction distance of the catalyst bed from the propellant surface. There is a minimum critical distance from the surface of the propellant that the catalyst bed must be withdrawn so that the catalyst no longer has any effect on the combustion process.

(U) The critical distance was calculated from a series of tests conducted in an internal Northrop program. It appears to be a slight function of chamber pressure (the higher the chamber pressure the greater the critical distance) as described by the equation below (for pressures between 200 and 1200 psia):

$$d_c = 0.585 + 0.0125 \frac{P_c}{1000}$$
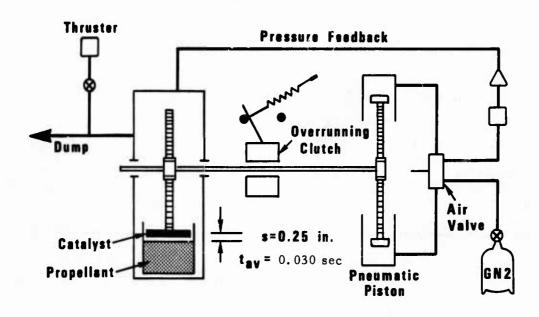
Figure 39 - Functional Schematic of 12-Inch-Diameter Test
Gas Generator   (U)

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where:

d_c = critical distance, in.

P_c = chamber pressure, psia

Table XXVI - 12-Inch Test Gas Generator Torque Requirements (U)

Force to Overcome	Value	Torque (in. -lb)
Rotational Mass Moment of Inertia	$0.0006\ lb_m\text{-sec}^2\text{ft}$	4.5
Linear Mass Moment of Inertia	$0.37\ lb_m\text{-sec}^2$	11.0
Friction		6.2
Weight to be Lifted (catalyst bed and rack)	$7.1\ lb_m$	6.2
Spring Force (overrunning clutch)	$7.0\ lb_f$	9.7
System Efficiency	75 percent	12.4
Contingency		10.0
	Total	60.0

(U) Whereas the critical distance establishes the minimum distance the catalyst must be retracted (approximately 0.06 inch), consideration must be given to the maximum distance to retract the catalyst. The further the catalyst is retracted from the propellant surface, the greater the variation in chamber pressure due to control response time. Computer runs were made with retraction distances of 0.25 and 0.10 inch. The results showed a 3 percent increase in pressure undershoot for the 0.25 inch retraction distance as compared to the 0.10 inch retraction distance. Based on these runs, a catalyst retraction distance of 0.10 inch was established.

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(U) The importance of lag time is shown in Figure 40.
Lag time is defined as the interval between the time the signal
to move the catalyst is generated and the time the catalyst begins
to move.   The initiation of catalyst movement is the time the
output shaft of the motor reaches 90 percent maximum torque.
Figure 40, Mass Flow Variation, further shows the relationship
between the percent variation in generator mass flow (overshoot
or undershoot from nominal), average catalyst velocity, lag time,
and generator mass flow.   The percentage mass flow shown is
mass flow at which the generator is operating, compared to the
maximum capability of the generator.   Figure 40 is applicable
to steady state bi-stable operating conditions and assumes that
all burning augmentation is caused by catalytic action.   Transient
burning rate augmentation experienced when the withdrawn catalyst
is replaced on the grain is not considered in Figure 40.   It also
shows that when the average catalyst velocities are in the range
of five inches per second or greater, and the lag time is in the
range of 20 to 50 milliseconds, lag time has the primary effect
on the percentage mass flow variation and increases in average
catalyst velocity have minimal effect.

Table XXVII below, summarizes the control system performance
requirements.

<u>Table XXVII - Control System Requirements</u> (U)

Characteristic	Requirement
Travel Distance (inch)	0. 10
Lag Time (second)	0. 020
Catalyst Retraction Time (second)	0. 020
Torque (in. -lb)	60
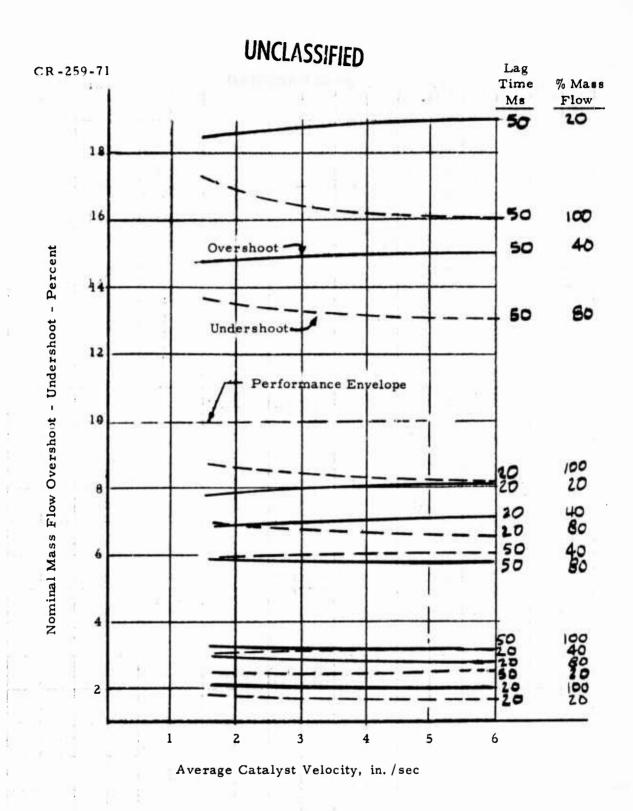
Figure 40. Mass Flow Variations (U)

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d. Candidate Systems

(U) Potential control system techniques were investigated to determine their ability to move the catalyst onto and away from the propellant surface. Techniques analytically investigated were:

1. Pneumatic
   - Chamber warm gas
   - External cold gas
2. Hydraulic
   - Electrically controlled
3. Electrical
   - DC stepping motor
   - DC Motor with magnetic particle clutch
   - DC motor with fast response start up characteristics.

(U) The control systems were rated on their ability to provide, 1) positive direction control, 2) rapid catalyst movement, 3) restricted withdrawal distance, 4) quick response needed for catalyst movement, 5) insensitivity to g-forces and gas temperatures, 6) low external power requirements, and 7) ease of fabrication and implementation, with minimum weight and envelope.

(U) In order to provide data for selecting the three most promising systems, literature surveys were requested from the Defense Documentation Center and the Science and Technology Research Center at Research Triangle Park, N. C., on pneumatic reversible rotary actuators. Literature on hydraulic and electric control actuators was solicited directly from the aerospace industry. The documents and literature received were analyzed in order to establish the initial suitability of major control system components for the DGG system. A rating matrix was developed for evaluating each type of actuator based on the aforementioned pertinent

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characteristics. As shown in Table XXVIII,each type of actuator
was given a rating of 1, 2 or 3, in increasing order of desirability.
The warm gas pneumatic system was clearly superior, with the
hydraulic and printed-circuit motor (d-c motor with fast response
start up characteristics) electrical system rating nearly the same
but second and third respectively, to the pneumatic system.

(U) The basic elements of the three candidate systems are
described in the following paragraphs.

• Hydraulic Control System

As shown in Figure 41, the hydraulic control system
consists of a power source which may be electro-hydraulic
or pneumatic-hydraulic; a four-way hydraulic motor; and an
overrunning clutch which is coupled to the catalyst position
gear shaft.

The electric command signal for up or down movement
of the catalyst actuates the four-way hydraulic valve which
in turn controls the direction of rotation of the hydraulic
motor. The hydraulic motor drives the catalyst against
the propellant surface on the "down" command. On the
"up" command (reversal of the hydraulic motor), the travel
of the catalyst is limited by the overrunning clutch. The
overrunning clutch is used on all the control systems to limit
catalyst retraction distance.

• Pneumatic Control System (U)

(U) The pneumatic control system is similar to the
hydraulic system except for the working fluid. The pneumatic
system utilizes warm gas from the gas generator or cold gas
from a stored gas system to drive a rotary motor which
transmits torque to the output gear shaft. To provide torque

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TABLE XXVIII - CONTROL SYSTEM RATING MATRIX (U)

CHARACTERISTIC	ELECTRIC (DC)			HYDRAULIC	PNEUMATIC	
	Stepping Motor	Motor and Clutch	Printed Circuit Motor	(All Systems)	Stored Cold Gas	Warm Gas
FUNCTIONAL ADAPTABILITY	1	1	2	3	3	3
MEETS PERFORMANCE REQUIREMENTS			✓	✓	✓	✓
FLIGHTWEIGHT POTENTIAL			1	3	1	3
RELIABILITY			2	2	2	3
LONG-TERM STORAGE			3	2	2	3
ENERGY REQUIREMENT (DRIVE POWER)			2	2	1	3
COMPATIBILITY WITH MISSILE POWER SYSTEM			3	2	1	3
ENVELOPE			2	2	1	3
AVAILABILITY OF TEST WEIGHT UNIT			✓	✓	✓	✓
TOTAL	—	—	15	16	11	21

Based on analysis and literature by:

Aerospace Fluid Component Design Handbook; WADD Tech Rep 449; AMC Pamphlet 706-138/139;
SEG-TR 65-22 (Bendix); AFFDL-TR 66-184 (Bendix); 'Control Engineering'; Kidde Aerospace Div;
Kidde Co (Hot Gas Control Systems); General Dynamics (Electric and Pneumatic Actuators for Aerospace).
an ASME Publication

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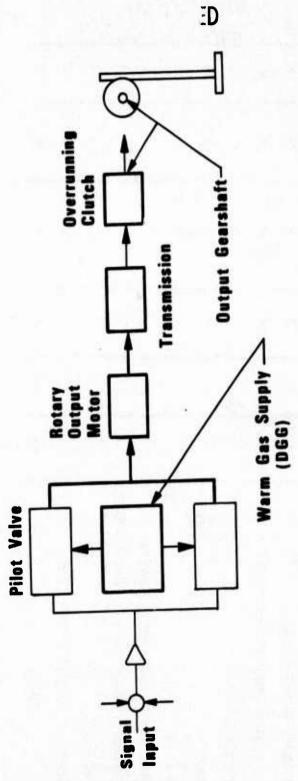
Figure 41 - Pneumatic Control System Schematic (U)

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reversal, pilot valves are operated which direct the gas flow through the actuator.

As the analysis of the pneumatic control system progressed it became evident that the proposed warm gas turbo pneumatic actuator could not meet the response time of the control system.

● Electric Control System (U)

(U) Basically the system consists of a d-c motor coupled to the catalyst gear shaft. A gear box reduces the motor speed to increase the torque output to the catalyst gear shaft. A control signal provides the proper polarity to rotate the motor in one direction or the other to raise or lower the catalyst.

(U) As shown by Table XXVIII, three types of d-c motor drives were initially considered. As the analysis of the actuator systems progressed, it became evident that the d-c stepping motor, and d-c motor with the magnetic particle clutch systems were functionally inferior to the printed circuit d-c motor and were dropped from further consideration. The d-c stepping motor was dropped due to its precise incremental travel distances. This is not compatible with variable flow demands on the gas generator which may require a variation in distance the catalyst must travel to the propellant surface. The d-c motor with the magnetic clutch was discarded due to the complexity of the unit as compared to the printed circuit motor.

e. Gas Generator Performance Analysis (U)

(U) In order to verify overall gas generator performance with the four selected control systems, NCI conducted computer studies

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with its math model DGG program.   Table XXIX is a summary
of the performance data.   The following inputs, computer runs,
were made at volume to surface (v/s) ratios of 3, 5, and 7 for
the four control systems.

(U)   <u>Grain and Propellant</u>

Characteristic Velocity, C^*	=	3600 ft/sec
Molecular Weight	=	20.40
Flame Temperature	=	$2450^\circ R$
Density	=	0.0527 lb/in.^{3}
Burn Surface	=	237.20 in.^{2}

(U)   <u>Pressure</u>

Nominal	=	600 psia
Upper Control	=	603 psia
Lower Control	=	597 psia

(U)   Figure 42 is a replot of a computer run to show the
effect of v/s ratio on the gas generator performance at mass
flow rates of 12.5 and 90 percent of nominal flow rate with the
hydraulic control system.   Figures 43 and 44 represent similar
effects of v/s ratio on the electrical and turbo-pneumatic control
system. Of the three systems, the electrical control system
provides the best overall gas generator system performance
whereas the turbo-pneumatic control system results in the greatest
mass flow and pressure variations.

(U)   The band width for the average pressure mass flow
variation for the 12.5 percent nominal mass flow rates in Figures
42, 43, and 44 is a result of two factors:

1.   The assumed gas demand "on" times are 0.250 second
at this flow level.

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TABLE XXIX

DATA ON THE CATALYST ACTUATION ASSEMBLY (12 IN. D.G.G. COLD GAS TESTS) (U)
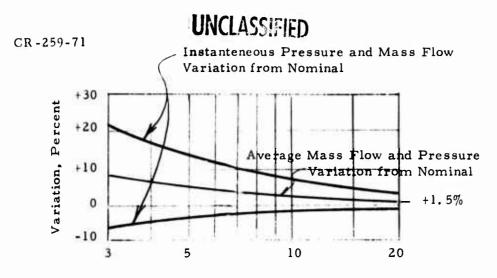
Test No.	12 Inch Generator Pressure psi	V/S	Lag In MS On	Off	Catalyst Travel Time MS	Power Consumption HP	Remarks
HCG-6 -5 -4	800	7 5 3			10.7/10		Oil hydraulic actuator MIL-H 5606 at △P 2000 psi catalyst cycle-rate 10 cps (5 on-off, 6 off-on) catalyst travel dist. 0.1 in.
HCG-3 -2 -1	400	7 5 3	*+ 17/8	*+ 47/8	10/10	.6/1.72	
SA 3581	Ambient	3			9.4/10		
ECG-1 -3 -5	800	3 5 7				.45/.67	Electric actuator 36 VDC catalyst cycle rate 20 CPS (10 on-off, 10 off-on) catalyst travel dist. 0.1 in.
ECG-2 -4 -6	400	3 5 7	± @ 4/1	4.5/1	10.5/15		
ECG-4a	Ambient	5				.42/.67	

* Valve + 3 MS mech. lag spring returned commercial solenoid valve.
+ Obtainable with aerospace type valve mech. lag not included.
± Incl. mech. lag of 3 MS (typ).
@ Mech. lag of 3 MS not included (typ).
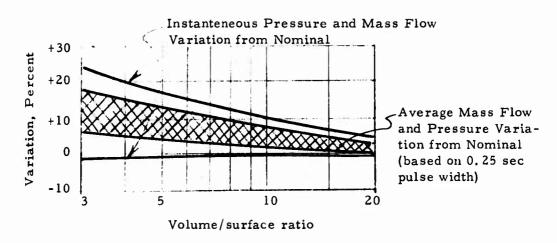
Measured / Predicted

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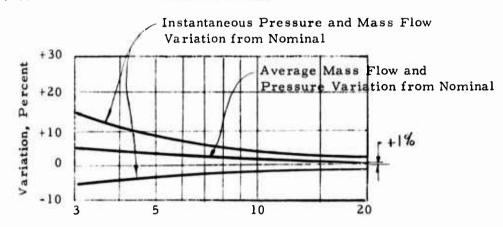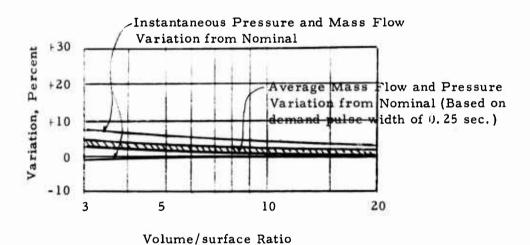
Figure 42 - Mass Flow and Pressure Variation Characteristics
for the Proposed Hydraulic and Warm Gas (Recipro-
cating) Control Systems   (U)

Volume/surface Ratio

90 Percent Demand Mass Flow Level

Volume/surface Ratio
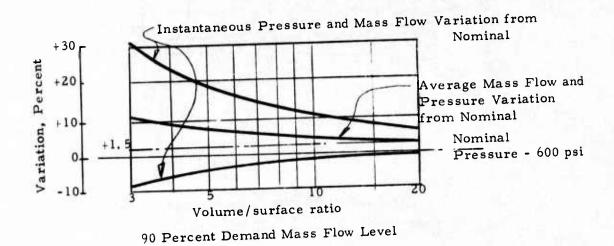
12.5 Percent Demand Mass Flow Level

Figure 43. Mass Flow and Pressure Variation
Characteristics for the Proposed
Electrical Control System   (U)

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90 Percent Demand Mass Flow Level

12.5 Percent Demand Mass Flow Level
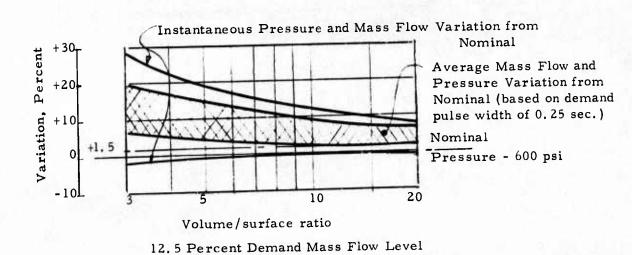
Figure 44 - Mass Flow and Pressure Variation Characteristics
for Proposed Warm Gas (turbine) Control System (U)

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2. The gas generator pressure decay time (lapsed time between cycles when catalyst is down on propellant surface) exceeds 0.250 second and is as high as 0.45 second for the hydraulic control system at a v/s ratio of 3.

Thus, the 0.250 second gas demand may be taken during the initial phase of gas generator pressure decay (catalyst removed from propellant) or at the tail end of the gas generator pressure decay (just prior to return of the catalyst on the propellant). Figure 45 illustrates this relationship.
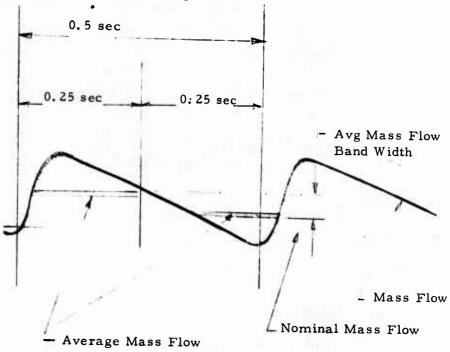
Figure 45 - Average Mass Flow Band Width Analysis (U)

(U) As noted by Figures 42, 43 and 44, the band width of the mass flow variation from nominal decreases as v/s increases since the amplitude of the mass flow variation decreases as v/s increases.

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(U) It should be pointed out that the Demand Gas Generator pressure and mass flow variation can be adjusted so that the average pressure and mass flow are the nominal desired levels regardless of the v/s ratio. This feature is illustrated by Figures 46 and 47.
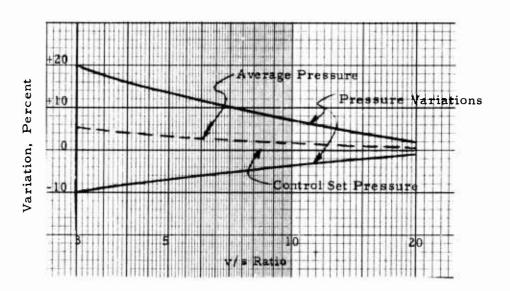
Figure 46 - Gas Generator Pressure Variation with Fixed
Control Set Pressure   (U)

(U) By incorporating a gas generator pressure feedback loop into the control circuit, it is possible to sense generator average pressure and adjust the control set pressure to a lower pressure than nominal which will lower the generator average pressure to the desired nominal pressure. From Figure 46 above it is apparent that in order to bring the generator average pressure to the nominal pressure at a v/s = 3, the control set pressure must be 5 percent below the nominal value. As the grain surface burns

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back and the v/s increases, the control set pressure must be
changed upward to compensate for the decreasing variation in
generator average pressure from nominal. Thus, to achieve a
constant generator average pressure (and also mass flow rate),
as the v/s ratio increases, the control set pressure must be
continuously changed to a pressure lower than the desired nominal
pressure by the amount that the generator average pressure is
above the nominal desired pressure. This is illustrated in
Figure 47 below.
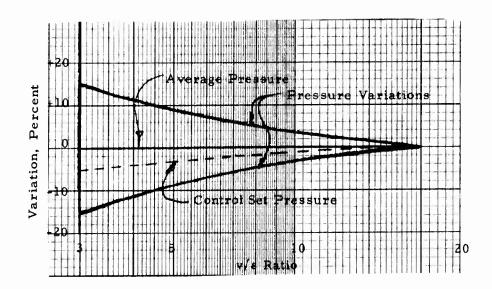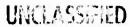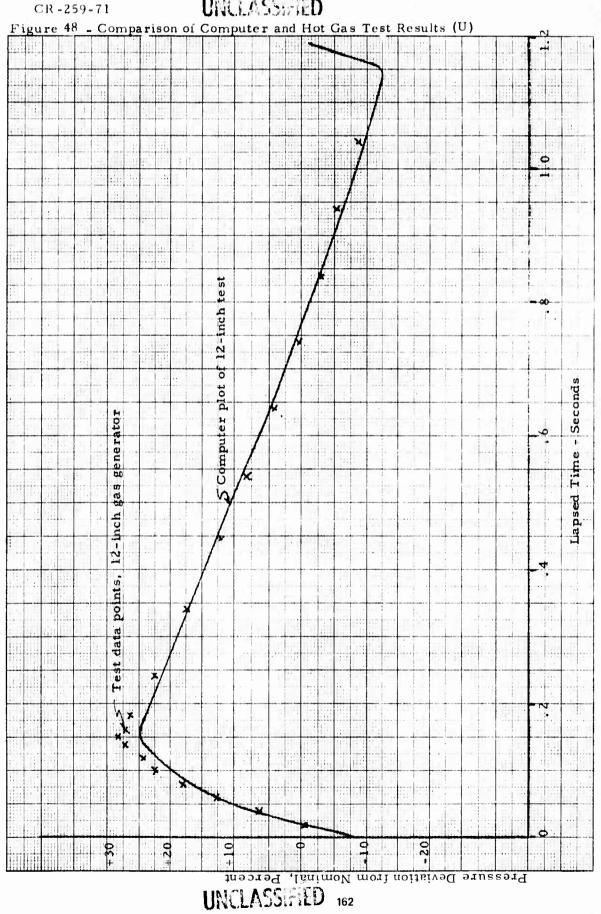
Figure 47 - Effect of Changing Control Set Pressure on
Gas Generator Average Pressure (U)

(U) The math model Demand Gas Generator computer program,
developed under previous company sponsored programs is based upon
analysis and Demand Gas Generator test results. Figure 48 is a

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Figure 48 - Comparison of Computer and Hot Gas Test Results (U)

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plot of pressures for a computer run and an actual 12-inch gas generator test. The closeness of the actual test results to the predicted results are indicative of the validity of NCI's Demand Gas Generator computer math model.

f. Thrust Motor Performance Analysis (U)

(U) To evaluate the effect of the control system operation on a dual chamber motor, NCI conducted a dual chamber computer program with the following inputs:

(U) Gas Generator

Propellant	R-500
V/s ratio	3
Chamber pressure, psia	600
Mass flow, nominal, lb/sec	1.0
Control system	Hydraulic

(U) Thrust Motor

Propellant	OX-1
Mass flow, lb/sec	4
Chamber pressure, nominal, psia	100
L^*, inch	413

(U) Figure 49 is a plot of the gas generator mass flow rate and thrust motor pressure profile as a function of time for the computer run. This figure shows that at the worst gas generator operating point of a v/s of 3, the average pressure variation in the aft thrust chamber is 2.5 percent from nominal.

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Figure 49 - Thrust Motor Pressure Trace (U)

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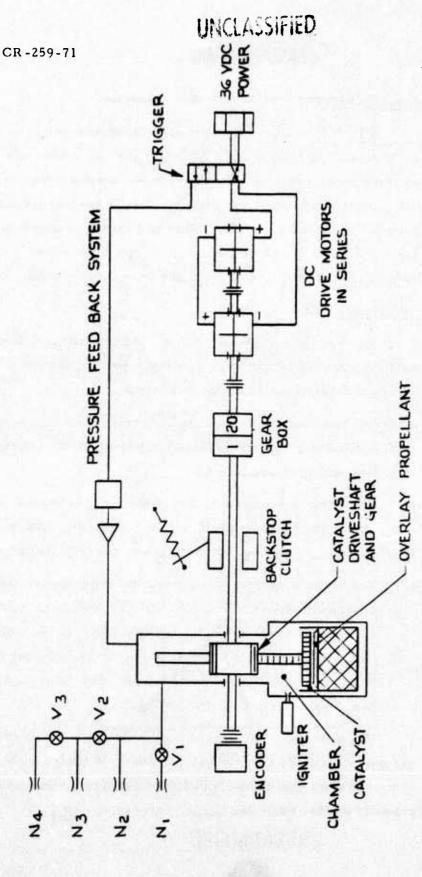
g.   Control Tests (U)

(U) The results of the control mechanism cold gas tests are compiled in Table XXIX. All warm gas and system tests were performed with the electrical control system. Figure 50 shows schematically the test bed and its control system hookup. Figures 51, 52 and 53 show amplitudes of pressure (over and under shots) for a set control pressure under varying mass flow rates as a function of control response.

h.   Conclusions (U)

(U) From the literature survey, gas generator system analysis, and the Demand Gas Generator math model computer runs, the following conclusions were made:

- Bistable operation of the three control systems provides a relatively constant generator pressure at various mass flow and pressure levels.

- The warm gas control system is the most attractive from the standpoint of adaptability, weight, reliability, long-term storage, energy requirement (power source), and envelope.

- The electric control system, with the high torque, fast response, reliable d-c motor actuator, offers the best control system by providing constant gas generator pressure modulation over a wide range of v/s ratios and mass flow levels. The turbo-pneumatic actuator offered the least desirable system from this standpoint.

(U) Scaleability of the constant pressure, variable mass flow gas generator from a three-inch diameter to a twelve-inch diameter control system was demonstrated and no evidence was found to preclude further scale-up.

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FIGURE 70. -12-INCH DIAMETER DEMAND GAS GENERATOR FUNCTIONAL SCHEMATIC (U)

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SYSTEM CONTROLS AT 100% $\dot{m}$ (THROTTLING RATIO = 1)
3, 6 & 12 DENOTES RATIO OF V/S

PLENUM
PRESSURE
OVERSHOT

+30%
+20%
+10%
0
-10%

PLENUM
PRESSURE
UNDERSHOT
FROM SET
CONTROL PRESSURE

0 2 4 6 8 10 12 14 16

TIME IN MS TO CATALYST MOVEMENT (LAG TIME)

DGG PRESSURE (MAX & MIN) AS A FUNCTION OF LAG TIME (U)

FIGURE 51

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SYSTEM CONTROLS AT 20% $\dot{m}$ (THROTTLING RATIO = 5)
4 DENOTES RATIO OF V/S

TIME IN MS TO CATALYST MOVEMENT (LAG TIME)

DGG PRESSURE (MAX & MIN) AS A FUNCTION OF LAG TIME (U)

FIGURE 52

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SYSTEM CONTROLS AT 10% $\dot{m}$ (THROTTLING RATIO = 10)
4, 8 & 12 DENOTES RATIO OF V/S

DGG PRESSURE (MAX & MIN) AS A FUNCTION OF LAG TIME (U)
FIGURE 53

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(U) The propellant burning rate reaction time is short enough to allow burn rate change as rapidly as the catalyst position can be changed.

9. SYSTEM TESTS (U)

    a.   Introduction (U)
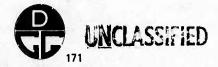
        (U) The objectives of the eight, twelve-inch diameter gas generator system tests were to determine:

- (U) The reliability of the generator components, i. e. control system, catalyst bed, ignition sub-system, propellant, manifolds, and valves

- (U) The maximum throttling ratio of the gas generator with R-500 pressed propellant; initial goal = 10/1

- (U) The response of the control system to pressure changes

- (U) The ability of the gas generator to operate for long durations, i. e. 400 seconds or longer

- (U) The ability of the gas generator to perform multiple short pulses of a simulated post-boost propulsion duty cycle

- (U) The ability of the gas generator to operate at different pressure levels

- (U) The long duration activity of the catalyst when constantly on the propellant.

        (U) All of these sufficient objectives were accomplished in the twelve-inch diameter gas generator test vehicle.

    b.   Approach (U)

        (U) The approach of the system tests was to attempt each new performance objective while using proven components. Each duty
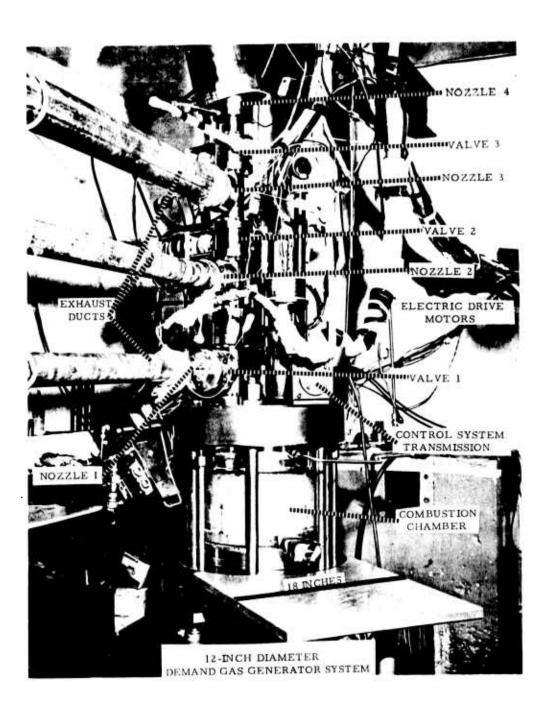
cycle included a repeat of a previously accomplished objective before its procession to a new objective.
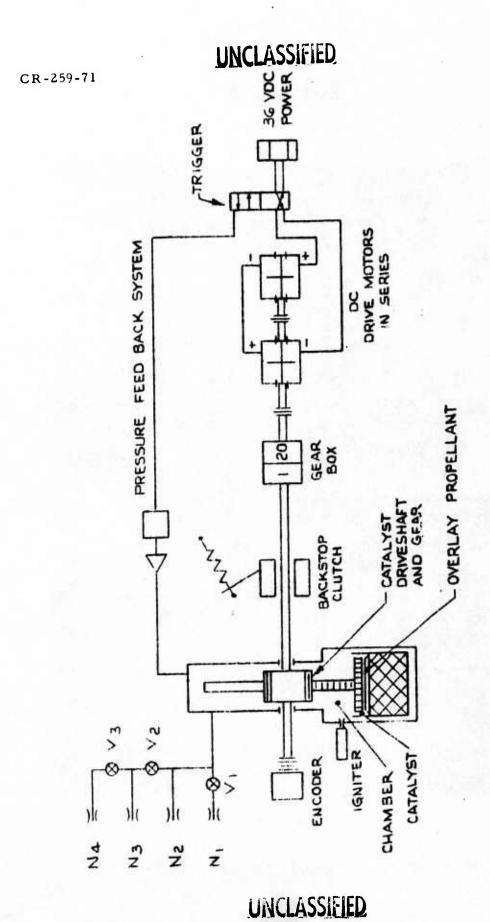
(U) The twelve-inch diameter gas generator assembly is shown in Figure 54. Changes to this basic design were made only when dictated by a performance failure or duty cycle requirements. A functional schematic of the generator assembly is shown in Figure 55. After Tests 15 and 16, which were the first two system tests, Valve 3 and Nozzle 4 were added due to the duty cycle requirements.

(U) The basic twelve-inch diameter gas generator test bed configuration was fabricated and assembled per Northrop Carolina Drawing Number 043-10197. This unit was mounted vertically as shown in Figure 54. The gas generator chamber consisted of a heavyweight top plate to which was mounted the exhaust port manifold with its valves, nozzles, and ducting, the electrical controller drive motors, the catalyst bed transmission, a safety blowout port, and associated plumbing. The aft closure or bottom of the chamber consisted of a heavyweight movable (hydraulically actuated) plate. A barrel which contained the R-500 propellant and insulation formed the cylindrical walls of the gas generator chamber. The igniter was mounted to the top or forward longitudinal section outer diameter of the chamber cylindrical wall. The assembly was bolted together with tie rods.

(U) The electronics for the controller, the manual control for opening and closing the valves, the data acquisition system, the 36-volt electrical supply for the drive motors and the firing system were contained in the test control room. A data acquisition test list and instrument measuring accuracies are given in Table XXX.

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Figure 54 -

Twelve-Inch Diameter Demand Gas Generator System (U)

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Figure 5.5 -

Twelve-Inch Diameter Demand Gas Generator Functional Schematic (U)

TABLE XXX   -   INSTRUMENTATION LIST (U)

Parameter and Location	Range	Code	Accuracy
Pressure			
Chamber	0-2000 psi	P_c	
Igniter	0-5000 psi	P_i	
Nozzle 1	0-2000 psi	P_{n_1}	±0.25%
Nozzle 2	0-2000 psi	P_{n_2}	
Nozzle 3	0-2000 psi	P_{n_3}	
Temperature, Probes			
Chamber	0-2500°F	$T_{p,c}$	
Nozzle 1	0-2500°F	T_{p,n_1}	±1.73%
Nozzle 2	0-2500°F	T_{p,n_2}	
Nozzle 3	0-2500°F	T_{p,n_3}	
Nozzle 4	0-2500°F	T_{p,n_4}	
Temperature, Surface			
Valve 1	0-1000°F	T_{s,v_1}	
Valve 2	0-1000°F	T_{s,v_2}	
Valve 3	0-1000°F	T_{s,v_2}	
Manifold	0-1000°F	$T_{s,m}$	
Valve Position Potentiometer			
Valve 1		Pos_{v_1}	
Valve 2		Pos_{v_2}	
Catalyst Position Potentiometer			
Catalyst Drive Gear		Pos_{cat}	±0.0005 inch
Ignition Current		V_i	

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c. Tests (U)

(U) The objectives of each successive system test increased in complexity upon successful completion of each test. Following is a listing of the tests, the test objectives, and accomplishments made during the system tests. All tests were in the twelve-inch diameter gas generator test vehicle.

(1) Test 15 (U)

(U) The objectives of Test 15 were: 1) to repeat the successful ignition accomplished in Test 14, 2) to determine the amount of catalyst deactivation when using Grade II R-500 propellant, 3) to demonstrate controller durability, 4) to demonstrate bistable control at a constant pressure, and 5) to determine three equilibrium K_n-pressure points of the Grade II R-500 propellant.

(U) Accomplishments of Test 15 were:

- Satisfactory ignition

- Test duration: 194 seconds

- K_n-pressure data obtained on Grade II R-500 propellant

(U) A post-test inspection of the catalyst bed showed that approximately 75 percent of the catalyst bed had been contaminated. An ash determination of that portion of the grain burned during the pressure degradation was 0.070 percent. Grains with ash contents in the 0.070 percent level were therefore determined to be undesirable for use. Three K_n design points (2000, 1500, and 781) for grains with 0.070 percent ash were determined. Little or no further

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degradation in pressure occurred after approximately
64 seconds, showing that at the 0.70 percent ash level
in the propellant, there is an equilibrium point where little
further contamination occurs.

(2)   Test 16 (U)

(U) The objectives of Test 16 were: 1) to demonstrate
the satisfactory ignitions of Tests 14 and 15, 2) to deter-
mine the amount of catalyst deactivation occurring when
using Grade III R-500 propellant with the catalyst in the
constant down mode of operation, 3) to demonstrate con-
troller durability, 4) to demonstrate bistable control at a
constant pressure, and 5) to obtain two K_n-pressure points
of the Grade III R-500 propellant in the twelve-inch diameter
generator.

(U) The accomplishments of Test 16 were:

- Satisfactory ignition

- Test duration: 170 seconds

- Bistable operation for 41 seconds at
  90 percent maximum mass flow rate

- No contamination on the catalyst bed

- Throttling ratio of 1.33 obtained

- Successful termination of grain by
  raising catalyst bed

(3)   Test 17 (U)

(U) The objectives of Test 17 were: 1) to evaluate

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the capability of the gas generator, catalyst, and controller to operate in the bistable mode for an extended period of time in the bistable mode, 2) to repeat bistable control of 90 percent maximum mass flow rate demonstrated in Test 16, 3) to check bistable control at a throttling ratio of 5 to 1, 4) to provide for a satisfactory ignition phase, and 5) to evaluate a modified manifold assembly.

(U) The accomplishments of Test 17 were:

- Satisfactory ignition

- Test duration: 20 seconds

- Verification of K_n-pressure design point

- Exhaust duct cooling system was found to be the cause that shorted out the control system during the tests.

(U) The controller electronics were shorted out immediately after R-500 ignition and the test was terminated at 20 seconds.

(U) A post-test inspection of the generator showed that the water aspirator used to help duct the exhaust gases from the test bay had begun spraying the generator at three seconds when Valve 1 was closed. The water had covered the electrical connections to the control system motors. All of the instrumentation and controller electronics were wet. It was concluded that the control system had failed to operate due to the water either shorting out the motors or the electrical leads to them. After the motors and electrical leads were dried out, the control system was functioned and performed

satisfactorily. Corrective measures were instituted to correct the test problems. The water aspirator was eliminated, and the ducting was modified to provide for easier exhausting of the gases. An electrical check of the visual chamber pressure gage was instituted to insure its proper operation.

(4)   Test 18 (U)

(U) The objectives, design, and configuration of Test 18 were the same as those of Test 17 except corrective action was taken to prevent shorting out of electronic equipment.

(U) The accomplishments of Test 18 were:

● Satisfactory ignition

● Test duration: 150 seconds

● Ninety-second bistable control at ninety percent maximum mass flow rate

● Forty seconds of bistable control at a 5-to-1 throttling ratio

● Response times of control systems from command signal to execution was 20 to 25 milliseconds.

(U) There were some irregularities in the control cycles caused by noise in the electronic circuit, but it did not cause pressure abnormalities.

(5)   Test 19 (U)

(U) The objectives of Test 19 were: 1) to repeat the capability to operate at a 5-to-1 throttling ratio, 2) to demonstrate the ability to operate at a 10-to-1 throttling ratio, and 3) to evaluate the performance of a longer manifold assembly.

(U) The accomplishments of Test 19 were:

- Satisfactory ignition

- Test duration: 102 seconds

- Demonstrated a throttling ratio of 5 to 1

- Obtained a throttling ratio of 10 to 1 for six seconds.

(6)   Test 20 (U)

(U) The objectives of Test 20 were: 1) to repeat the capability of operating at one-fifth maximum mass flow, 2) to demonstrate the ability to operate for periods longer than six seconds at one-tenth maximum mass flow, 3) to ignite the gas generator satisfactorily, and 4) to operate in the bistable mode for an extended period of time.

(U) The accomplishments of Test 20 were:

- Satisfactory ignition

- Test duration: 184 seconds

- Bistable operation for 180 seconds

- Demonstrated the throttling ratio of 5 to 1
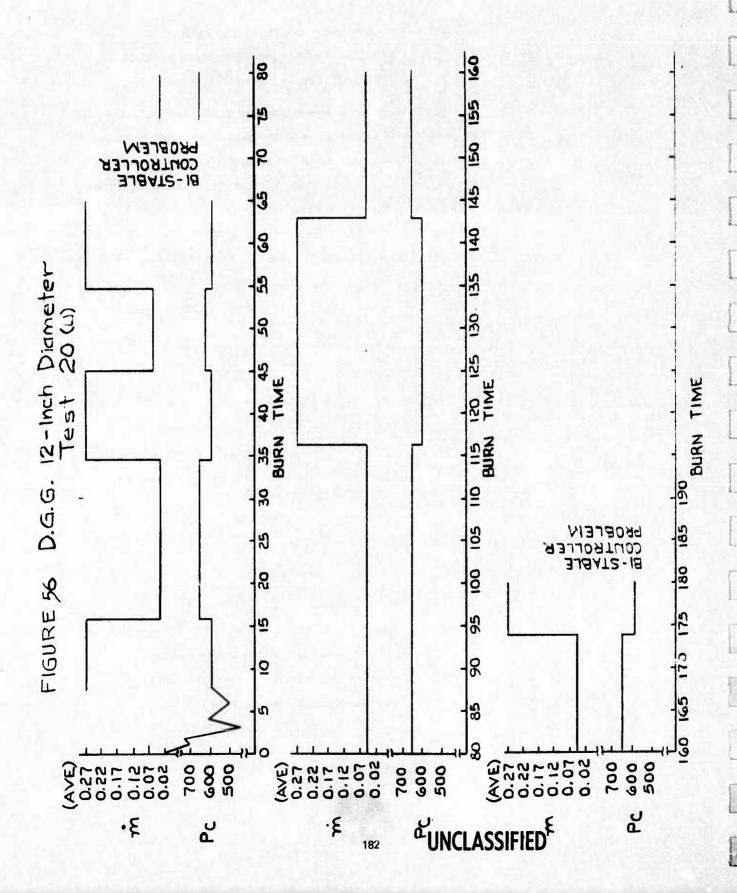
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- Demonstrated the throttling ratio of
  10 to 1 at three separate demand periods
  of 20-, 40-, and 50-second duration.

(U) Figure 56 shows delivered mass flow rate and
gas generator chamber pressure as a function of time for
Test 20. The only abnormality experienced was from
64.4 seconds to 75.0 seconds when the bistable controller
ceased to operate and an abnormally high pressure occurred.
At 180 to 184 seconds, the controller again operated improp-
erly giving a wide pressure band width just before termina-
tion. Test 20 represents a significant milestone in achieving
an approximate 10-to-1 throttling ratio, and 180 seconds of
bistable operation.

(7) Test 21 (U)

(U) The objectives of Test 21 were: 1) to repeat the
capability of operating the gas generator at one-tenth maxi-
mum mass flow, 2) to check the capability to operate at one-
sixteenth maximum mass flow, and 3) to ignite the gas
generator satisfactorily.

(U) The accomplishments of Test 21 were:

- Satisfactory ignition

- Test duration: 280 seconds

- Signals to the drive motor were not clear
  which negated accomplishments of the
  primary objectives. A secondary objec-
  tive obtained was examination of the
  catalyst bed after 280 seconds of

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FIGURE 56 D.G.G. 12-Inch Diameter Test 20 (u)

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significant chamber pressure variation.
No contamination or loss of catalyst
material was detected.

(U) A review of the data from Test 21 showed that
many command signals from the controller to the electric
drive motor were not clear enough to command the motors
to turn in either one direction or the other. As a result,
the catalyst was never fully retracted during bistable opera-
tion. In other cases, there was a series of alternate up-and-
down commands which lasted from 30 to 50 milliseconds.
In these cases, the catalyst remained stationary and the pro-
pellant simply burning away from the catalyst bed. Through-
out the test, these alternate commands at a minimum delayed
the catalyst response, and caused a much wider control pres-
sure band that had been seen previously. The slower response
times and lack of full catalyst retraction prevented the achieve-
ment of any throttling ratio demonstration during this test.
An analysis of the problem showed that it was the result of an
electrical feedback from the lines between the controller and
electric motors. These lines supply electrical power to the
motors. When a power pulse was supplied to the electric
motors, an electromotive force was created in the command
lines which connect the pressure transducer to the controller.
This created a false and opposite command signal to the one which
was given to the motors. This in turn created another false
command signal. This electrical feedback problem was
created by putting all of the electronic wiring in bundles. It
was corrected by separating the power lines to the electrical

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motors from the rest of the electrical lines. This change
was evaluated in a checkout procedure which provides,
under simulated operating conditions, readings of the
voltage, amperage, and command signals to the electric
motors and the response time and force to the catalyst bed
from the electric motors. The checkout was run with the
motor chamber pressure at atmospheric and at 600 psi. No
problems were encountered in either case.

(8) Test 22 (U)

(U) The objectives of Test 22 were: 1) to evaluate the
gas generator operation at a throttling ratio of 10 to 1,
2) to check the capability to operate at a throttling ratio of
16 to 1, and 3) to ignite the gas generator satisfactorily.

(U) The accomplishments of Test 22 were:

● Cause of unsatisfactory ignition was
found to be improper catalyst positioning

● Total test duration: 284 seconds.

(9) Test 23 (U)
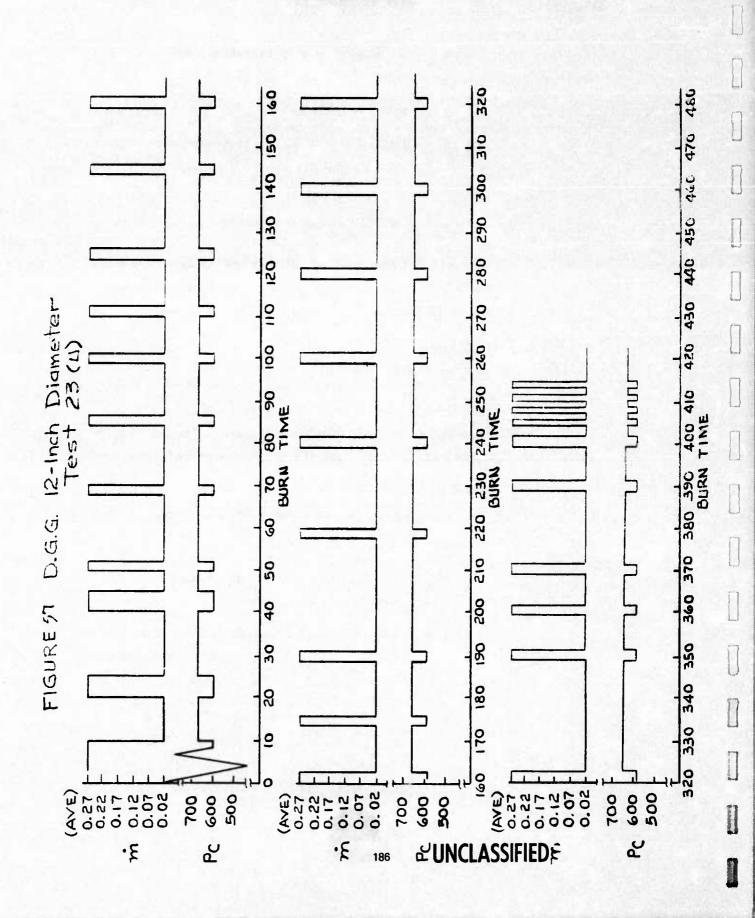
(U) The objectives of Test 23 were: 1) to ignite the gas
generator successfully, and 2) to evaluate the gas generator
operation at a throttling ratio of 10 to 1 during a simulated
post-boost propulsion duty cycle.

(U) The accomplishments of Test 23 were:

● Satisfactory ignition

● Test duration of 420 seconds in
bistable operation

- Demonstrated a 10-to-1 throttling
  ratio

- Ran for 29 cycles

- Four short maximum mass flow rate
  cycles, approximately one-second
  duration each

- Successful termination

(U) Figure 57 shows delivered mass flow rate and
gas generator chamber pressure as a function of time
for the simulated post-boost propulsion duty cycle.

(10)   Test 24 (U)

(U) The objectives of Test 24 were: 1) to satisfactorily
ignite the gas generator, and 2) to evaluate gas generator
capabilities to operate at throttling ratios from 6 to 1   to
16 to 1 while controlling at chamber pressures of 600, 400,
and 200 psia.

(U) The accomplishments of Test 24 were:

- Satisfactory ignition

- Test duration of 357 seconds bistable
  operation

- Demonstrated a throttling ratio of 16 to 1
  at eight separate demand periods of 3, 60
  10, 17, 10, 20, 10, and 7 seconds

- Demonstrated a throttling ratio of 6 to 1
  at four separate demand periods of 20, 10,
  8 and 6 seconds

FIGURE 57 D.G.G. 12-Inch Diameter Test 23 (4)

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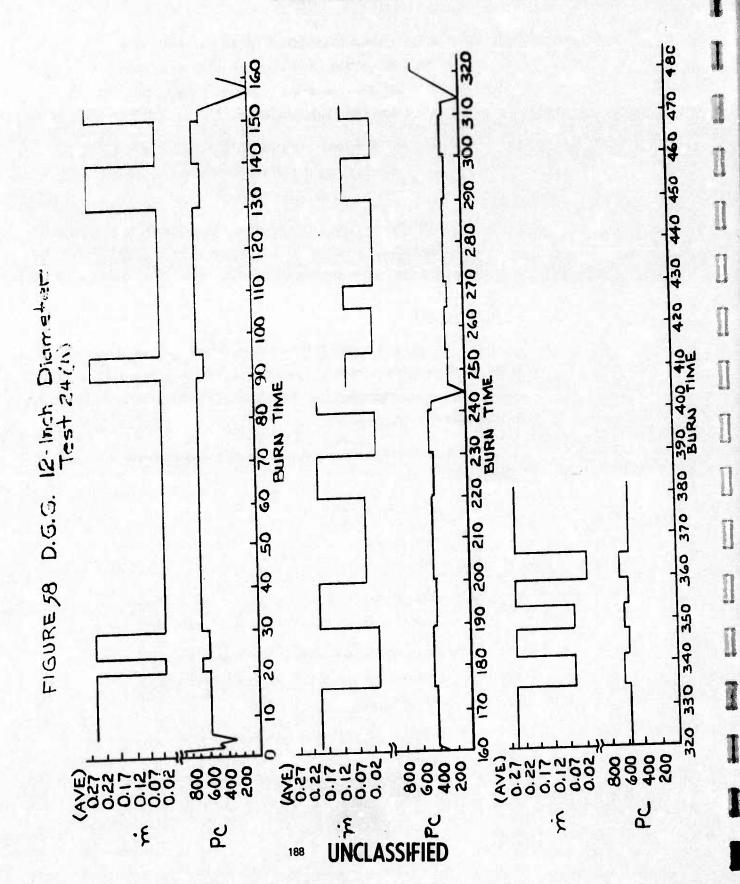
- Demonstrated full mass flow, one-sixth mass flow, and one-sixteenth mass flow at three separate pressure levels of 600, 400 and 200 psia

- Demonstrated a throttling ratio of 38 to 1 by changing operating pressure levels from a maximum of 600 psia.

(U) Figure 58 shows delivered mass flow rate and gas generator chamber pressure as a function of time for Test 24.

d. Conclusions (U)

(U) The program objectives were achieved and the viability of the solid propellant demand gas generator concept for application to post-boost propulsion systems was demonstrated in twelve-inch diameter test hardware.

(U) Significant achievements of the ten-system tests included:

1. Satisfactory ignition

2. Test durations in the bistable mode up to 420 seconds

3. Mass flow ratios up to 16 to 1 at any constant chamber pressure between 200 and 600 psia

4. Mass flow ratios as high as 38 to 1 when the chamber pressure was varied between 200 and 600 psia

5. Catalyst control system response of 20 to 25 milliseconds.

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FIGURE 58 D.G.G. 12-Inch Diameter Test 24(N)

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SECTION V - DEVELOPMENT OF
AN IMPROVED PROPELLANT SYSTEM (CASTABLE) (U)

1. INTRODUCTION (U)

*(U) Efforts to develop an improved guanidine nitrate propellant and an improved chromic oxide catalyst were conducted in parallel to the baseline system development. The overall objective of the propellant improvement program was the development of a demand gas generator propellant with performance, processing, and mechanical property characteristics comparable to those of a conventional gas generator propellant. The size and configuration of baseline propellant grains are limited since that propellant is compression molded. The specific impulse of the baseline propellant both alone and in combination with thrust motor propellants is less than conventional gas generator propellants. Also, the optimum mixture ratio of the baseline propellant with thrust motor propellants is below that of conventional propellants.

(U) The improved propellant program was directed toward the development of a castable composition with a polymeric binder. Such a propellant could be cast in essentially unlimited sizes and configurations, would have improved elastomeric mechanical properties, and could be formulated with an auxiliary oxidizer to give improved specific impulse and optimum mixture ratio values.

*(U) The overall objective of the improved catalyst program was the development of a reproducible chromic oxide catalyst which would withstand the temperature-pressure environment of the gas generator. The baseline catalyst is formed by thermal decomposition of ammonium dichromate on stainless steel screens coated with a nickel aluminum alloy.

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Techniques other than thermal decomposition of ammonium di-
chromate were investigated for coating the screens with chromic oxide.
These include plasma spray and electrophoretic decomposition.

2.   PROPELLANT DEVELOPMENT (U)

    a.   Introduction (U)

        (U) The objectives of this task were to develop and charac-
terize two castable composite propellants which satisfy the pro-
gram requirement given in Table XXXI.

        *(U) The approach taken consisted of using guanidine nitrate
in combination with 1) a fluid binder to provide castability and
elastomeric properties to the cured propellant and 2) an auxiliary
oxidizer such as ammonium perchlorate to obtain a clean burning
composition.

    b.   Literature Survey (U)

        (1)   Binders (U)

            *(U) Three basic type binders were considered for the
program.   These were 1) materials which would decompose
catalytically in the presence of hot chromic oxide, 2) inert
materials which would give high pressure deflagration
limits and low burning rates with conventional oxidizers,
and 3) conventional solid propellant binders which give good
mechanical properties to the propellant.   The following
polymers were selected for evaluation:

        1.   Catalytically decomposable

- 2-methyl 5-vinyl tetrazole:
  acrylic acid copolymer

- 2-methyl 5-vinyl tetrazole:
  hydroxyethyl methacrylate

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TABLE XXXI

CASTABLE PROPELLANT REQUIREMENTS (U)

- Density (lb/cu in.)   ≥ 0.049

- Flame Temperature (°F)   1800-2200

- Theoretical Specific Impulse, 40:1, vac.

    Gas Generator (M.R. = 0)   ≥ 210

    Combination with OX-1 (M.R. ≥ 2.0)   ≥ 270

    Combination with TP-F-1006
    (M.R. ≥ 3.0)   ≥ 270

- Catalyzed Burning Rate (in./sec)   0.04 to 0.30

- Throttling Ratio, 500-1000 psi   ≥ 10:1

- Mechanical Properties @ 70°F

    Maximum Stress (psi)   ≥ 100

    Strain at Maximum Stress (in./in.)   ≥ 0.20

- Processable by Conventional Methods

2. Inert

- C_7 fluoroacrylate (duPont)
- FC-2202 (3M Company)

3. Conventional

- F-17-80 polyester (Witco)
- HC-434 carboxy-terminated polybutadiene (Thiokol)
- R-45M hydroxy-terminated polybutadiene (Atlantic-Richfield)

(U) Three types of curing agents, i.e. epoxides, aziridines, and isocyanates, were selected for evaluation with the above prepolymers. The C_7 fluoroacrylate is a monomer which cures via vinyl polymerization. Benzoyl peroxide and dichlorobenzoyl peroxide were selected as catalysts for the initiation of C_7 fluoroacrylate cure process.

(2) Guanidine Nitrate* (U)

*(U) Commercial sources and grades of guanidine nitrate were also identified in the literature survey. American Cyanamid, which produces a commercial grade of 91 to 92 percent purity, was selected as the guanidine nitrate source. The as-received material was purified into three grades prior to use since the effect of impurities, primarily ammonium nitrate and melamine, on ballistic and physical properties was unknown. The purification steps are outlined below.

Grade I

- Dried at 100°-110°C for 24 hours
- Micropulverized

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Grade II

- Washed with 1. 5 parts water at 10° - 15^OC

- Filtered and slurry washed with 0. 2 parts acetone

- Dried at 100° - 110^OC for 16 hours

- Micropulverized

Grade III

- Dissolved in three parts water at 70° - 80^OC

- Filtered to remove water insolubles

- Cooled to 20^OC for recrystallization

- Filtered and washed with 0. 2 parts acetone

- Dried at 100° - 110^OC for 16 hours

*(U) Typical properties of three grades of guanidine nitrate are given in Table XXXII.

c. Compatibility Studies (U)

*(U) Compatibility tests were conducted using differential scanning calorimetry to determine the reactivity at evaluated temperatures of each grade of guanidine nitrate with the curing agents listed in Table XXXIII. The following conclusions were drawn from these tests.

- Reactivity increased with increasing temperature.

- Reactivity of guanidine nitrate decreased with increasing purity.

- Relative reactivity of the three types of curing agents was: isocyanates > aziridines > epoxides.

*(U) The compatibility of Grade III guanidine nitrate and ammonium perchlorate with these curing agents was further investigated by determining degree and rate of cure of propellant

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TABLE XXXII - PROPERTIES OF GUANIDINE NITRATE*(C)

Property	As Received	Grade I	Grade II	Grade III
Composition (Wt. %)				
Guanidine Nitrate				
Wet Analysis	91.58	92.33	98.68	99.61
DSC	---	---	96.01	98.96
Ammonium Nitrate	6.09	4.04	0.87	0.18
Melamine	1.48	1.48	0.62	0.13
Volatiles	0.45	0.15	0.11	0.05
pH, 10% Aqueous Solution	6.79	4.49	4.35	4.12
Melting Point (°C)	189-205	199-201	209-212	212-214
Heat of Fusion (cal/gm)	---	---	34.4	43.6
Heat of Combustion (cal/gm)	---	1862.	1687.	1633.

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TABLE XXXIII-CURING AGENTS (U)

Compatibility[*]

A. CARBOXY-TERMINATED POLYMER CURING AGENTS

Epoxides

ERL-0510	triglycidyl p-aminophenol	C
ERL-4206	vinylcyclohexene dioxide	MR
ERL-4221	3,4-epoxycyclohexyl methyl-3,4-epoxycyclohexene carboxylate	C
ERL-4201	3,4-epoxy-6-methylcyclohexyl methyl-3,4-epoxy-6-methyl cyclohexane carboxylate	C
EPON-812	1,2,3-tris (2,3-epoxy propoxy) propane	MR
DEN-438	poly phenol formaldehyde poly (2,3-epoxy-propyl) ether	MR
DER-332	diglycidyl ether of bisphenol-A	C

Aziridines

MAPO	tris 1-(2-methyl) aziridinyl phosphine oxide	MR
HX-868	trifunctional aromatic aziridine	MR
HX-740	difunctional aliphatic aziridine	MR

B. HYDROXY-TERMINATED POLYMER CURING AGENTS

Isocyanates

TDI	toluene diisocyanate	NC
HDI	hexamethylene diisocyanate	MR
DDI	diisocyanate derivative of dimevic fatty acid	MR
PAPI	polymethylene polyphenyl isocyanate	NC

*C = compatible; MR = mild reaction; NC = not compatible

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formulations containing 40 percent solids loading. Of nine curing agents studied for the HC-434 prepolymer systems, only MAPO, ERL-0510, and HX-868 gave acceptable cure. The physical properties of these formulations were superior to those of R-45M propellants.

(U) Only ERL-0510 and DEN-438 gave acceptable cure with the polyester prepolymer, F17-80. Of these two curing agents, ERL-0510 offered greater flexibility toward adjusting physical properties with the polymer to curing agent stoichiometry and demonstrated greater stability to accelerated aging.

(U) Only ERL-0510 demonstrated a reasonable pot life with the 2-methyl 5-vinyl tetrazole: acrylic acid prepolymer and also gave comparable mechanical properties to propellant cure with MAPO, HX-868, EPON-812 or DEN-438. Severe gassing problems were encountered with the hydroxy-terminated tetrazole prepolymer cured with isocyanates.

(U) On the basis of these studies, the hydroxy-terminated prepolymers were eliminated from consideration and the following binder systems were selected.

Type	Polymer	Curative
Polybutadiene	HC-434	HX-868 or ERL-0510
Polyester	F17-80	ERL-0510
Tetrazole	2MVT:AA	ERL-0510

C_7 fluoroacrylate monomer cured with dichlorobenzoyl peroxide was chosen as the fluorocarbon binder based on availability and knowledge of this system.

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d. Formulation Limitations (U)
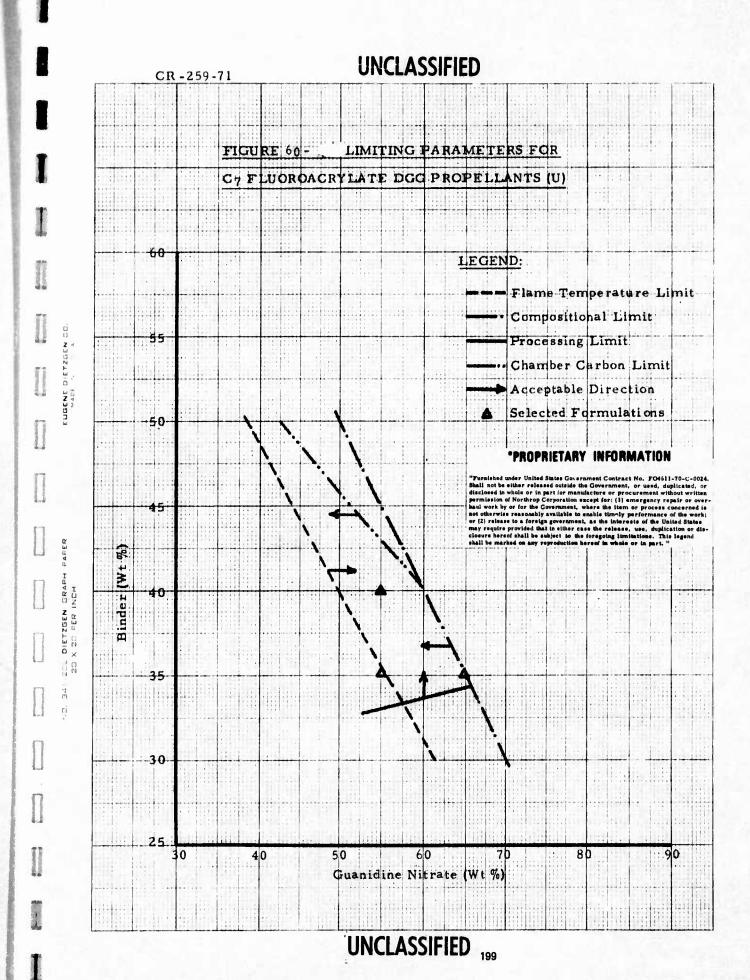
(U) Processing studies were conducted to establish the maximum total solids loading to retain castability with each of four binder systems. A bimodal oxidizer blend of 60 percent 20-50 micron and 40 percent 400-micron particles was used. The ammonium perchlorate in the formulation was incorporated as part of the fine fraction of the blend. The small ammonium perchlorate had less surface area and wetted easier than fine guanidine nitrate. The maximum solids content processable with the polybutadiene binder was 79 percent, with the polyester 75 percent, with the fluorocarbon 65 percent, and with the tetrazole 60 percent. Viscosities at the end of mix ranged up to 15 kilopoises.

*(U) Higher solids loading could have undoubtedly been obtained using spherical guanidine nitrate and/or trimodal blends. However, no effort was made on this program to evaluate these approaches.

(U) The theoretical performance limits of the compositions were established with thermochemical calculations for gas generator formulations and in combination with two dual-chamber, thrust motor propellants, TP-F-1006 and OX-1.

(U) From the processing and thermochemical data, formulation limits for achievement of the program requirements were established for each propellant system. These are shown in graphical form in Figures 59 through 62. Lines of specific impulse, chamber carbon density, flame temperature, processing limits are plotted as functions of composition. The balance of the propellant composition at any point is percent ammonium perchlorate.

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FIGURE 59 -

LIMITING PARAMETERS FOR CTPB PROPELLANTS (U)

LEGEND:

Specific Impulse Limit
Density Limit
Solid Carbon Limit
Processing Limit
Flame Temperature Limit
Acceptable Direction
Selected Compositions

Guanidine Nitrate (Wt %)

Binder (Wt %)

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FIGURE 60- LIMITING PARAMETERS FOR C7 FLUOROACRYLATE DGG PROPELLANTS (U)

LEGEND:

— — Flame Temperature Limit
— · — Compositional Limit
——— Processing Limit
— · · — Chamber Carbon Limit
——▶ Acceptable Direction
▲ Selected Formulations

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Binder (Wt %)

Guanidine Nitrate (Wt %)

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FIGURE 61 -

LIMITING PARAMETERS FOR POLYESTER

DGG PROPELLANTS (U)

*PROPRIETARY INFORMATION

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LEGEND:

▲ Selected Formulations
—— · — Chamber Carbon Limit
— — — Flame Temperature Limit
— · · — Specific Impulse Limit
— · — Density Limit
——— Processing Limit
——▶ Acceptable Direction

Binder (Wt %)

Guanidine Nitrate (Wt %)

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FIGURE 62 --- LIMITING PARAMETERS FOR TETRAZOLE PROPELLANTS (U)

LEGEND:

— · — Density Limit
— — — Flame Temperature Limit
— · · — Composition Limit
— · · · — Chamber Carbon Limit
——— Processing Limit
→ Acceptable Direction
▲ Selected Compositions

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e. Selection of Two Propellant Systems (U)

(U) The ballistic properties of at least two formulations of each of the four propellant systems were determined in three-inch diameter motors. The formulations evaluated are denoted by triangles in Figures 59 through 62. Catalyzed and noncatalyzed burning rates, chamber temperatures and characteristic velocity were measured in a total of 48 tests. The composition and characteristics of one formulation of each propellant system are given in Table XXXIV.

(U) The polybutadiene propellant system demonstrated all the physical property and ballistic requirements of the program with the exception of throttling ratio.

(U) The fluorocarbon system met all program requirements using the physical properties of aged propellant. It was concluded that the fluorocarbon as well as the polybutadiene propellants were not completely cured at the end of seven-day cure cycles since improved properties were obtained on additional cure.

(U) The polyester propellant system met each of the program requirements except throttling ratio and density. Propellant density could be increased to the required value but throttling ratio is far below the objective, and it is unlikely that composition change can sufficiently increase the ratio to the required level.

(U) The tetrazole propellant would require considerable effort to reach the development stage of the other systems. Motor tests with the tetrazole propellants were unsuccessful resulting either in overpressurization or extremely low pressure

TABLE XXXIV—CHARACTERISTICS OF FOUR PROPELLANT SYSTEMS (U)

Propellant Type	Polybutadiene	Fluorocarbon	Polyester	Tetrazole
Composition (Wt. %)	HC-434 19.34	C_7 30.32	F17-80 26.00	2MVT:AA 14.36
	HX-868 1.41	Viton A 3.00	ERL-0510 3.75	TEGDN 24.41
	Lecithin 0.25	DCBP 1.05	Lecithin 0.25	ERL-0510 1.23
	GN 30.00	HEM 0.63	GN 45.00	GN 40.00
	AP 49.00	GN 55.00	AP 25.00	AP 20.00
		AP 10.00		
Physical Properties				
Density (lb/cu. in.)	0.052	0.054	0.048	0.051
End-of-Mix Viscosity (Kp/°F)+	11/118	8.6/80	3.6/140	2.2/108
Maximum Stress (psi)+	195	133	110	34
Strain @ Max. Stress (in./in.)+	0.55	0.28	0.32	0.04
Modulus (psi)+	887	863	585	---
Thermochemical Properties				
Flame Temperature (°F)	1970	2078	1780	2100
Isp, GG, 40:1 Vacuum	225	220	210	227
Isp. TP-F-1006	288	283	278	286
Optimum MR	3.0	2.5	3.0	3.0
Isp. OX-1	287	276	275	285
Optimum MR	2.0	1.5	1.5	2.0
Ballistic Properties				
r_b @ 500 psi, noncatalyzed	0.046	0.0024	0.058	0.15*
r_b @ 500 psi, catalyzed	0.275	0.0395	0.126	---
Throttling Ratio	6 to 1	16.5 to 1	2.2 to 1	---*
r_b Exponent, noncatalyzed	0.05	---	---	0.78*
r_b Exponent, catalyzed	0.12	0.90	0.67	---

* Strand Data

+ Following 30-day storage at 150°F

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operation. The malfunction of these tests may have been caused
by a pattern of low density lines in the grains revealed by X-ray.
Tetrazole propellants may have future application in high mass
flow rate gas generators where a high burning rate is advantageous.

(U) The polybutadiene and fluorocarbon propellant systems
were chosen for further development based on the degree to
which the physical and ballistic characteristics of these systems
approached the program requirements.

3. ADVANCED FLUOROCARBON PROPELLANT DEVELOPMENT (U)

a. General (U)

(U) The objectives of this effort were to completely define
the catalyzed and noncatalyzed burning rates of the fluorocarbon
propellant and improve its processing characteristics. A portion
of the fluoroacrylate monomer was lost during mixing, casting,
and initial cure due to the volatility of the monomer and the cure
time of the propellant was exceedingly long, i.e. thirty days.

b. Cure Characterization (U)

(U) The effect of various factors on the cure rate and ulti-
mate mechanical properties of the fluorocarbon propellant systems
was investigated. These factors included 1) the concentration
and type of cure catalyst, 2) the removal of inhibitor from the
C_7 fluoroacrylate and hydroxyethyl methacrylate monomers,
3) the cure temperature cycle, and 4) the inhibiting effect of oxygen
and guanidine nitrate on the cure rate.

(1) Effect of Cure Catalyst (U)

(U) Gumstock studies with the fluorocarbon binder and
each of the catalysts, dichlorobenzoyl peroxide and benzoyl

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peroxide, indicated an optimum catalyst concentration of 0.6 percent of the binder. Concentrations above this level resulted in gassing, and lower concentrations gave very poor cures.

(U) Little difference was observed between the rate of cure obtained with the two catalysts as shown in Table XXXV. Because of the minor difference between the catalysts, benzoyl peroxide was chosen giving the following binder composition.

C_7 fluoroacrylate	88.7%
Viton A	8.9%
Hydroxyethyl methacrylate	1.8%
Benzoyl peroxide	0.6%

(2) Effect of Monomer Inhibitor (U)

(U) Both the C_7 fluoroacrylate and hydroxyethyl methacrylate contain a cure inhibitor after manufacture to increase shelf life. It was found that reduction in inhibitor level of hydroxyethyl methacrylate to 200 ppm and the complete removal of the C_7 fluoroacrylate inhibitor prior to propellant mixing increased cure rate as shown in Table XXXV. All subsequent mixes were made with the reduced inhibitor concentrations.

(3) Effect of Oxygen (U)
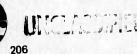
(U) Some vinyl polymerizations are known to be inhibited by oxygen in the air. Samples of mix E-750 were cured under nitrogen atmospheres of 13.7 and 30 psi. The results of these tests, also shown in Table XXXV indicate

TABLE XXXV - E-701 FLUOROACRYLATE PROPELLANT CURE RESULTS (U)

Mix No.	Cure Temp. (°F)	Cure Time (days)	Cure Catalyst	Monomer Inhibitor	Maximum Stress (psi)	Strain at Maximum Stress (in./in.)	Modulus (psi)
E-740	120	12	dichloro-benzoyl peroxide	present	28	0.12	610
	120	18			21	0.14	800
	120	25			35	0.21	1095
E-739	120	12	dichloro-benzoyl peroxide	removed	48	0.47	470
	120	18			54	0.41	1125
	120	25			58	0.47	960
E-750	120	12	benzoyl peroxide	removed	44	0.17	860
	120	25			57	0.25	1300
	120	25			70	0.51	705
	120	25			65	0.58	783

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an improvement in physical properties in the absence of oxygen. Curing under a nitrogen pressure of 30 psi showed no advantage over ambient pressure indicating that monomer was not lost due to volatilization at a cure temperature of $120^\circ F$.

(4) Effect of Guanidine Nitrate*(U)

*(U) Three, one-gallon mixes were manufactured for tensile properties studies to determine the effect of guanidine nitrate on cure. Two mixes, E-755 and E-762, consisted of the standard E-701 formulation. In the third mix, E-756, the guanidine nitrate was replaced with ammonium perchlorate while maintaining the same volume-solids loading level as E-701, i.e. 69 percent. The formulations are shown below and the tensile properties as a function of cure time are given in Table XXXVI.

	E-755 and E-762	E-756
C_7 fluoroacrylate	31.05	26.00
Viton A	3.11	2.60
Hydroxyethyl methacrylate	0.63	0.53
Benzoyl peroxide	0.21	0.17
Guanidine nitrate	55.00	---
Ammonium perchlorate	10.00	70.70

*(U) Tensile properties were measured at 5, 10, 15, and 40 days for E-755 and E-756 propellant cured at $120^\circ F$. The mix with guanidine nitrate cured as rapidly as that propellant containing only ammonium perchlorate indicating that guanidine nitrate does not inhibit the C_7 fluoroacrylate cure. The tensile properties of another guanidine nitrate mix, E-762, were measured after, 3, 5, 10, and 15 days of cure.

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TABLE XXXVI - EFFECT OF GUANIDINE NITRATE ON FLUOROCARBON PROPELLANT CURE (u)*

Mix No.	Oxidizers	Cure Time (days)	Maximum Stress (psi)	Strain at Maximum Stress (in./in.)	Modulus (psi)
E-755	GN and AP	5	65	0.31	903
		10	67	0.31	815
		15	61	0.21	515
		40	68	0.21	578
E-762	GN and AP	3	33	0.15	621
		5	42	0.18	586
		10	48	0.21	1050
		15	53	0.25	835
E-756	AP	5	44	0.12	1210
		10	47	0.11	1530
		15	46	0.12	628
		40	52	0.16	596

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In each case, ultimate mechanical properties were obtained after ten days of cure.

(5) Effect of Binder Components (U)

(U) The effect of C_7 fluroacrylate lot of raw material, Viton A, and hydroxy ethyl methacrylate on cure rate was determined by viscosity-time measurements of gumstocks using benzoyl peroxide catalysts. The following four samples were investigated.

1. C_7 fluoroacrylate monomer, Lot 6, used in all previous formulations

2. C_7 fluoroacrylate monomer, Lot 0915

3. C_7 fluoroacrylate monomer, Lot 6/Viton A

4. C_7 fluoroacrylate monomer, Lot 6/ hydroxyethyl methacrylate

The ratio of those binder components present in each sample was maintained the same as in E-701. The viscosity data showed no significant difference in cure rate of the two lots of C_7 monomer nor in the samples containing Viton A and hydroxyethyl methacrylate. All samples reached a maximum viscosity within 100 hours, indicating the cure reaction had stopped.

(U) A one-gallon mix of E-701 propellant was made with Lot 0915 C_7 monomer to verify the above results. Tensile properties were measured after 5, 10, and 15 days of cure at $120^{\circ}F$. The tensile property data are shown on the next page as a function of cure time.

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Cure Time (days)	Maximum Stress (psi)	Strain at Max. Stress (in./in.)	Modulus (psi)
5	46	0.30	473
10	46	0.21	660
15	53	0.22	709

The new lot of monomer did not change the rate of cure or improve the mechanical properties.

(6) Conclusions (U)

(U) Removal of the inhibitors from the C_7 monomer and hydroxyethyl methacrylate reduced the cure time of the fluorocarbon propellant to within ten days. Essentially 90 percent cure was achieved within five days. The other propellant components did not significantly affect the cure rate.

c. Ballistic Characterization (U)

(U) Additional three-inch motor tests were conducted to more accurately define the catalyzed and noncatalyzed burning rates of E-701 propellant. A closed motor chamber was used for noncatalyzed tests. The catalyst was periodically placed in contact with the grain to maintain a constant chamber pressure. This procedure gave a higher overall measured burning rate than the true noncatalyzed rate due to the catalyzed time and web consumed incorporated in the noncatalyzed value. The limiting noncatalyzed rate, which includes some catalyzed burn time, is a maximum value when used to calculate throttling ratio. A more accurate noncatalyzed rate is obtained by subtracting the portion of propellant consumed while the catalyst was in contact with the grain. However, this improved value is in error by the difference in

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the steady state catalyzed rate assumed for these time periods
and the catalyzed rate for the actual non-steady state conditions.

(U) The E-701 propellant burning rate data are presented
in Figure 63. Curves are plotted for both catalyzed and limiting
noncatalyzed burning rates. Data points are also shown for the
corrected noncatalyzed rates. A minimum throttling ratio of
17.4 to 1 was obtained from the limiting noncatalyzed curve.

d. Summary (U)

* (U) A summary of the final fluorocarbon propellant proper-
ties is given in Table XXXVII. The propellant met all of the pro-
gram objectives with the exception of maximum stress. It is be-
lieved that the mechanical properties of the propellant can be
improved by the use of a more spherical guanidine nitrate particle
and a cross-linking agent.

4. ADVANCED POLYBUTADIENE PROPELLANT DEVELOPMENT (U)

a. General (U)

(U) The polybutadiene propellant system initially developed
gave a short pot life of two to three hours at $130^{\circ}F$ and an unusually
long cure time exceeding two weeks at $140^{\circ}F$. The throttling
ratio of the characterized E-696 formulation was 6 to 1 which is below
the program requirement of 10 to 1. The objective of this effort
was to improve these characteristics without detrimentally affecting
other properties.

b. Cure Characteristics (U)

(U) Pot life and cure time of the polybutadiene propellant was
studied as a function of curing agent. ERL-0510 as the sole curative
and in combination with HX-868 in the ratios 3 to 1, 1 to 1, and

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FIGURE 63 - THREE-INCH MOTOR DATA FOR
E-701 FLUOROCARBON PROPELLANT (U)

TABLE XXXVII

CHARACTERISTICS OF E-701 PROPELLANT (U)

*Composition (Weight %)

C_7 fluoroacrylate	31.05
Viton A	3.11
Benzoyl peroxide	0.21
Hydroxyethyl methacrylate	0.63
Guanidine nitrate	55.00
Ammonium perchlorate	10.00

Physical Properties

End-of-mix viscosity (Kp @ $^{\circ}$F)	11 @ 80°
Density (lb/cu. in.)	0.054
Glass transition temperature ($^{\circ}$F)	-36
Pot life (hrs @ $^{\circ}$F)	>8 @ 120°

Tensile Properties

Cure Temp. ($^{\circ}$F)	Cure Time (days)	Maximum Stress (psi)	Strain @ Max. Stress (in./in.)	Modulus (psi)
120	5	65	0.31	903
	10	67	0.31	815
	15	61	0.21	515
	40	68	0.21	578

Thermochemical and Ballistic Properties

Isp, 40:1 vacuum	220
Chamber temperature ($^{\circ}$F)	2078
Burning rate @ 500 psia (in./sec)	
Catalyzed	0.040
Noncatalyzed	0.0023
Throttling ratio @ 500 psia	17.4
Burning rate exponent	
Catalyzed	0.92
Noncatalyzed	0.45
Onset of decomposition, DSC ($^{\circ}$C)	305.

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1 to 3 were evaluated. The pot life and mechanical properties as functions of cure time at $140^{\circ}F$ for E-696 propellant with the various curatives are given in Table XXXVIII. The viscosity-time data for the mixes showed that pot life increased as the proportion of ERL-0510 in the mixed curing agents increased. An acceptable pot life of six hours or greater was obtained with fifty percent or more ERL-0510.

(U) Ultimate tensile properties were not obtained within fifteen days with any of the propellants containing HX-868. When ERL-0510 alone or in combination with the cure catalyst stannous octoate was used, the tensile properties were essentially unchanged after ten days of cure. The ultimate properties were improved with the use of stannous octoate.

*(U) Similar results were obtained with a different ratio of guanidine nitrate to ammonium perchlorate as shown in Table XXXIX. The formulation containing HX-868 did not cure within 21 days; whereas, the ERL-0510 propellants were cured within seven days.

(U) It was concluded that an acceptable pot life and cure time could be achieved with ERL-0510 curing agent and with or without stannous octoate cure catalyst.

c. Ballistic Characteristics (U)

*(U) The original intent of this effort was to increase throttling ratio over the 6-to-1 value obtained with the E-696 formulation by adjusting the composition. However, midway through the project, results of the preliminary design study (see Section III) indicated that throttling ratio, if above 4 to 1, was not as critical a parameter with respect to weight of the propulsion system as the catalyzed burning rate of the polybutadiene propellant. Lower propulsion

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TABLE XXXVIII POT LIFE AND CURE PROPERTIES
OF POLYBUTADIENE PROPELLANT (U)

Mix No.	Curing Agent	Pot Life (hours)	Cure Time (days)	Maximum Stress (psi)	Strain at Maximum Stress (in./in.)	Modulus (psi)
E-736	HX-868	2-3	5	74	0.43	505
			10	79	0.39	375
			15	97	0.33	468
E-729	3/1 HX-868/ERL-0510	4	5	62	0.52	215
			10	110	0.39	458
			15	117	0.35	520
E-730	1/1 HX-868/ERL-0510	6	5	51	0.63	147
			10	166	0.35	665
			15	164	0.28	690
E-731	1/3 HX-868/ERL-0510	>6	5	119	0.45	313
			10	137	0.36	498
			15	144	0.28	690
E-735	ERL-0510	>7	5	134	0.23	970
			10	154	0.19	1180
			15	156	0.17	1380
E-737	ERL-0510 with stannous octoate	>7	5	170	0.35	1175
			10	188	0.24	1280
			15	188	0.24	1368

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TABLE XXXIX - EFFECT OF CURING AGENT

ON TENSILE PROPERTIES OF POLYBUTADIENE PROPELLANTS (U)

	E-696	E-758	E-757	E-745
* Composition (Wt. %)				
HC-434	19.34	18.95	19.46	19.37
ERL-0510	---	---	1.29	1.28
HX-868	1.41	1.80	---	---
Stannous octoate	---	---	---	0.10
Lecithin	0.25	0.25	0.25	0.25
Guanidine nitrate	30.00	36.00	36.00	36.00
Ammonium perchlorate	49.00	43.00	43.00	43.00
End-of-Mix Viscosity (Kp @ °F)	11 @ 118	13 @ 140	15 @ 140	10 @ 130
Cure Time (days)	7	7	7	7
Maximum stress (psi)	92	18	239	205
Strain @ max. stress (in./in.)	0.56	0.58	0.13	0.26
Modulus (psi)	520	176	2113	1355
Cure Time (days)	30	21	---	---
Maximum stress (psi)	195	67	---	---
Strain @ max. stress (in./in.)	0.55	0.50	---	---
Modulus (psi)	887	430	---	---

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weights were obtained in the design study with burning rates of
0. 10 in./sec than with rates above 0. 20 in. /sec as in the case of
E-696.   Therefore, composition modifications which would have
resulted in higher catalyzed burning rates such as increased
ammonium perchlorate content were not explored.   The variables
investigated were 1) the effect of increased guanidine nitrate con-
tent at the expense of ammonium perchlorate, 2) the effect of in-
creased binder content at the expense of ammonium perchlorate,
3) the effect of the curing agent changes adopted as a result of the
cure study, and 4) the effect of increased oxidizer particle size.

(U) The propellant formulations investigated are compared
with E-696 in Table   XL.   The catalyzed burning rates of the modified
formulations were reduced below that for E-696.   However, the
noncatalyzed rates were not reduced to the same degree resulting
in lower throttling ratios.   In fact, throttling ratio appears to be a
function of catalyzed burning rate.   A noncatalyzed burning rate for
E-761 was not obtained, unfortunately.   It appears that ERL-0510
gives a lower burning rate and throttling ratio than HX-868 com-
paring formulations E-757 and E-758.   The cure catalyst, stannous
octoate, increases burning rate and throttling ratio in formulation
E-745 compared with E-757.   The catalyzed burning rate can be re -
duced by oxidizer particle size change but the effect on throttling
ratio is not known.

d.   Conclusions (U)

* (U) Acceptable processing characteristics of the polybutadiene
propellant system were obtained with ERL-0510 in combination with
stannous octoate.   A pot life greater than seven hours and a cure

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TABLE - XL

BALLISTIC PROPERTIES OF POLYBUTADIENE PROPELLANTS (U)

Formulation Number	E-696	E-744	E-758	E-757	E-745	E-761
*Composition (Wt. %)						
HC-434	19.34	21.25	18.95	19.46	19.37	19.56
HX-868	1.41	---	1.80	---	---	---
ERL-0510	---	1.40	---	1.29	1.28	1.19
Stannous Octoate	---	---	---	---	0.10	---
Lecithin	0.25	0.25	0.25	0.25	0.25	0.25
Guanidine nitrate	30.00	30.00	36.00	36.00	36.00	30.00*
Ammonium perchlorate	49.00	47.00	43.00	43.00	43.00	49.00*
Ballistic Properties						
Flame Temperature (°F)	1975	1827	1826	1826	1826	1975
Isp, 40:1, vacuum (lb-sec/lb)	228	226	225	225	225	228
Burning Rate @ 500 psia (in./sec)						
Catalyzed	0.275	0.155	0.144	0.104	0.150	0.072
Noncatalyzed	0.046	0.033	0.033	0.027	0.033	---
Throttling Ratio @ 500 psia	6.0 to 1	4.7 to 1	4.3 to 1	3.8 to 1	4.5 to 1	---
Pressure Exponent (200-800 psia)						
Catalyzed	0.12	0.51	0.56	0.38	0.44	---
Noncatalyzed	0.05	0.07	0.18	0.61	0.14	---

*Particle size, 400 microns; all other compositions contain 60/40 blend of 20/400 microns.

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time within ten days were obtained. Reduction in catalyzed burning rate by increasing binder or guanidine nitrate at the expense of ammonium perchlorate was feasible. However, throttling ratio was reduced also. Design trade-off studies are necessary to determine if these changes are desirable from the standpoint of propulsion system weight.

5. LINER DEVELOPMENT (U)

a. Polybutadiene Propellant (U)

*(U) A liner consisting of forty percent guanidine nitrate and sixty percent binder was used for the three-inch motors with the polybutadiene propellant. Two liner compositions are given below with the corresponding mechanical properties.

Mix Number	F-277	F-281
Composition (Wt. %)		
HC-434	56. 19	56. 28
ERL-0510	3. 71	3. 72
Stannous Octoate	0. 10	---
Guanidine Nitrate (20 micron)	40. 00	40. 00
Mechanical Properties		
Maximum Stress (psi)	162	188
Strain at Max. Stress (in./in.)	0. 205	0. 290
Initial Modulus (psi)	1004	1035

b. Fluorocarbon Propellant (U)

* (U) The flurorcarbon propellant liner consisted of 35 percent guanidine nitrate and 65 percent binder as shown below.

C_7 fluoroacrylate	57. 66
Viton A	5. 78
Hydroxyethyl methacrylate	1. 17
Benzoyl peroxide	0. 39
Guanidine Nitrate (20 micron)	35. 00

Mechanical properties were not measured for the liner composition.

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6.   CATALYST DEVELOPMENT (U)

    a.   Introduction (U)

        *(U) Propellant burn rate changes in the demand gas generator are effected by placing the catalyst bed near or away from the grain surface. The design of the catalyst bed must be capable of performing its function at elevated temperatures for extended periods of time. This phase of demand gas generator development was concerned with identifying and testing numerous substrates or structures upon which the catalyst material could be mounted for function within the motor chamber, and with examining the catalyst surface area and how methods of application effect   the ballistic performance of the gas generator using previously characterized R-500 propellant.

    b.   Design and Approach (U)

        (1)   Standard Catalyst System (U)

            *(U) Initial investigations performed during Northrop Carolina Inc. 's OTA (overhead technical assistance) program on the Demand Gas Generator indicated that one of the primary problems in the catalyst system was catalyst flaking. Flaking is the cracking and subsequent dislodging of chromic oxide coating. Catalyst particles flaking from the substrate and falling onto the burn surface decrease the effectivity of controlling burn rate by withdrawing the main catalyst bed. The catalyst beds used on the OTA program were fabricated by the following process:

            o   (U) 12 x 12 mesh 304 stainless steel screen with a wire diameter of 0.025 inch was sand blasted at the Northrop Carolina, Inc. facility. The screens were degreased and sealed in polyethylene bags.

            o   (U) The screens were taken to a vendor facility and and a flame spray of chromium oxide was applied

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to a thickness of 0.005 to 0.010 inch.

- (U) The sprayed screen material was cut to size and dipped in a boiling solution of ammonium dichromate in distilled water, followed by firing over a M̧eaker burner which formed the desired chromium oxide. Excess loose chromium oxide was blown free.

(U) Investigations revealed that the flame spray primer applied to the support screen had debonded from the screen causing the flaking. Contributing factors were determined to be:

- (U) Incompatability of the linear coefficient of thermal expansion of the primer coat and the support wire mesh.

- (U) The primer was flame sprayed on the wire mesh in thicknesses of 0.005 to 0.010 inch. Review of available literature revealed that flame spray coatings of brittle ceramic materials should be controlled to a maximum thickness of 0.001 to 0.002 inch.

- (U) Surface preparation of the wire mesh prior to primer application.

*(U) Initial catalyst development effort was directed toward the above areas so that a standard catalyst could be established. Metco, Inc., a recognized authority in the field of flame and plasma spray coatings, was consulted, and the following changes were adopted:

- (U) Use a plasma spray process for application of the primer since it affords a greater selection of operational environments, temperature ranges and lends itself to improved process controls and reproducibility.

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- (U) Heat the stainless steel wire mesh prior to application of the plasma primer.

- (U) Continue to roughen the surface of the wire mesh prior to applying the primer but use aluminum oxide grit instead of sand.

- (U) Use a self-bonding material as the primer to be sprayed on the wire mesh prior to catalyst application. Self-bonding materials are those materials which provide microscopic bonding to the substrate (wire mesh).

(U) Two candidate spray materials decided upon. These were Metco 42C, a stainless steel material, and Metco 451, which is a nickel-chromium-aluminum material. It was further decided that the Metco 451 material would give the better results as it was developed as an alternate for Metco 42C to be used for applications that required high wear resistance and heavy build up with no damage or cracking. Also, as Metco 451 is sprayed, the nickel-aluminum reacts exothermically to produce semi-fused coatings of greater integrity than the Metco 42C.

- (U) Control the thickness of the Metco 451 plasma coating to 0.001 to 0.002 inch.

(U) The suggestions of Metco, Inc., were evaluated on samples of 12 x 12 mesh 304 stainless steel mesh screen with a wire diameter of 0.025 inch. The samples were prepared by aluminum oxide grit blasting the wire surfaces. Metco 451 was plasma sprayed on the steel screens to thicknesses of 0.001 to 0.010. The coated sample screens were subjected to bend tests and thermal cycling tests to determine if the plasma spray were solidly attached. It was found that screens with coating thicknesses

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less than 0.005 inch did not crack or flake during these tests, but that the samples with coating thicknesses or 0.006 inch or greater did crack but did not flake. These same tests were conducted on other samples of wire mesh which were prepared in the same manner but were preheated. After subjecting the samples to the same type bend and thermal tests, no detectable increase in plasma coating integrity was noticed.

*(U.) During these tests it was learned that increased thicknesses of the plasma spray coating resulted in increased surface roughness; a 210 microinch finish was obtained with a 0.005-inch spray thickness. Since the catalyst bed activity is dependent upon the surface area of the catalyst exposed, it was decided to use the coating thickness which yielded the greatest surface roughness without cracking or flaking. Metco 451 plasma spray thickness controlled between 0.003 and 0.005 inch satisfied these requirements.

(U) Upon completion of this effort, the standard catalyst was defined and the manufacturing procedure established. The manufacturing procedure is outlined in Table XLI.

(2) Other Candidate Catalyst Systems (U)

*(U) The objective of the catalyst development studies was to evaluate alternate chromic oxide catalyst bed systems which will withstand the temperature and physical environment in the demand gas generator chamber. The alternate systems were compared to the standard catalyst system to establish relative qualities for each.

(U) The standard catalyst system and the alternate catalyst systems were modified to cause variations in exposed catalyst surface area and determine the effect of these changes on the ballistic performance of the demand gas generator.

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TABLE XLI - MANUFACTURING PROCEDURE

FOR THE STANDARD CATALYST*(U)

1. 12 x 12 mesh 304 stainless steel mesh screen with a wire diameter of 0.025 inch is grit blasted with aluminum oxide.

2. The screen is then sent to a subcontractor, who applies a 0.003- to 0.005-inch plasma spray coat of Metco 451. (See data sheet in Appendix A.)

3. The coated screens are then die stamp cut to the desired dimensions for the 3-inch Demand Gas Generator test motor.

4. Three thicknesses of the cut screens are tightly wired together with nichrome wire.

5. The assembled screens are degreased in trichloroethylene and baked in a furnace at $1500^{\circ}F$ for ten minutes to assure removal of any contaminants.

6. The cleaned screen assemblies are immersed and left for two minutes in a boiling saturated solution of ammonium dichromate in distilled water.

7. The screen assemblies are then placed in an oven and dried for 30 minutes at $220^{\circ}F$. After this drying, the screens are uniformly coated with crystals of ammonium dichromate.

8. The beds are then placed in an electric furnace and baked for ten minutes at $1500^{\circ}F$. This brings about the decompositions of ammonium dichromate into chromic oxide, nitrogen and water as described by the following equation for the reaction.

$$(NH_4)_2 Cr_2 O_7 + Heat \longrightarrow Cr_2 O_3 + N_2 + H_2O$$

9. The excess chromic oxide formed in the manufacturing process is removed by spraying the catalyst bed with compressed dry air.

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*(U) The alternate systems evaluated were:

- (U) Chromic oxide plasma sprayed on stainless steel screen.

- (U) Oxidation of chromium plated screen or nichrome screen. (It was decided that both would be evaluated in initial investigations.)

- (U) Commercially available pellets of chromic oxide contained in a basket.

(U) A literature search was made and three authorities in the field of catalyst systems design and one in the field of filter materials were contacted for technical advice and recommended systems which would meet the Demand Gas Generator requirements. These contacts and their recommendations were:

- *(U) Battelle Memorial Institute, Ceramic Research Division, Columbus, Ohio, recommended two approaches. One was the bonding of chromic oxide to the wire substrate using phosphoric acid as a bonding intermediate. The advantage of this system was the relatively low (700°F) temperatures used in the application technique resulting in less degradation of the substrate or the chromium oxide. The second recommendation was the foaming of chromic oxide in a Hastelloy honeycomb support structure. This system affords a more rigid support and has the advantage of producing controlled and reproducible porosity.

- *(U) The Georgia Institute of Technology, Atlanta, Georgia, recommended the electrophoretic deposition technique. This system was suggested because of the low temperature (100°F) used in manufacture.

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The technique produces a chromium oxide coating which has good adhesion to wire screen substrate materials.

- *(U) Metco, Inc. , Westbury, New York, did not suggest any additional systems, but did make recommendations for improvements to the chromium oxide plasma spray process.

*(U) The above mentioned catalyst systems with exception of the commercially available chromic oxide pellets were evaluated in the initial phase of catalyst evaluation. The commercial pellets were not evaluated because a review of the tests accomplished on the OTA program revealed that these pellets could not withstand the thermal shock atmosphere of the gas generator chamber.

c. , Sample Preparation (U)

(U) A process was developed for preparation of each candidate catalyst system and this process was used for the manufacture of evaluation samples.

(1) Standard Catalyst (U)

(U) The samples of standard catalyst were manufactured in accordance with the process shown in Table XLI. A process procedure, NPS-1145, "Process Specification for Catalyst Bed Preparation," was prepared and implemented to control processing of the standard catalyst.

(2) Chromic Oxide Plasma Sprayed on Stainless Steel Screen *(C)

*(U) The chromic oxide plasma sprayed catalyst samples were fabricated by grit blasting 304 stainless steel with aluminum oxide and plasma spraying it with one coat of Metco 450 nickel-aluminum composite powder. The coated screens were then die stamp cut to size.

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(3) Oxidation of Nichrome Screen (U)

*(U) Catalyst samples of oxidized nichrome screen were fabricated of No. 5 nichrome alloy (80% nickel, 20% chromium) 16 x 16 mesh screen of a 0.020 inch wire diameter. This wire was placed in an electric furnace, with charcoal, heated to 1400°F causing rapid oxidation of the chromium in the wire producing the desired chromic oxide.

(4) Oxidation of Chromium Plated Screen (U)

*(U) Catalyst samples of 304 stainless steel screen, 12 x 12 mesh of a 0.025-inch diameter wire, were chromium plated by the standard electrodeposit technique. The plated screen was subjected to a heated atmosphere produced by an argon-hydrogen plasma. This created a hot oxidizing medium which accelerated the oxidation of the chromium plating, producing chromic oxide.

(5) Catalyst Pellets (U)

*(U) Previous attempts to press chromic oxide had indicated that the material was difficult to press in the pure form.

*(U) The studies conducted on this program were for the purpose of producing pellets of high chromic oxide content that would exhibit good physical and thermal properties. Pellets were pressed from pure chromic oxide with combinations of other materials selected because of their processing characteristics and compatibility. The results of these attempts are shown in Table XLII.

*(U) Effort in the catalyst pellet area was discontinued and the pellet type catalyst bed was not pursued further on this program because, (1) Commercially available pellets have not been found that will withstand the required thermal shock,

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TABLE XLII- RESULTS OF CATALYST PELLET PRESSING INVESTIGATION* (U)

	Pellets Pressed	Press Pressures (psi)	Vacuum (in. Hg)	Dwell Time (sec)	Remarks
Chromic Oxide	3	7,000	None	120	Pellets collapsed
Chromic Oxide	3	10,000	None	120	Pellets collapsed
Chromic Oxide	3	8,000	27	120	Pellets very soft
Chromic Oxide	2	24,000	27	120	Pellets broke in die
Chromic Oxide, 50% Silicon Dioxide, 50%	2	10,000	None	120	Pellets collapsed
Chromic Oxide, 50% Magnesium Oxide, 50%	2	10,000	None	120	Pellets very soft
Chromic Oxide, 50% Lead Oxide, 50%	2	10,000	None	120	Pellets very soft
Chromic Oxide, 50% Iron Oxide, 50%	2	10,000	None	120	Pellets very soft
Chromic Oxide Wire Reinforced	1	10,000	None	120	Pellet crumbled
Chromic Oxide, 80% Graphite, 20%	4	10,000	None	2	Pellets hard; properties good
Chromic Oxide, 85% Graphite, 15%	4	10,000	None	2	Pellets had good hardness
Chromic Oxide, 90% Graphite, 10%	2	10,000	None	2	Pellets looked good; edges soft
Chromic Oxide, 85% Graphite, 15%	2	24,000	27	2	Pellets had good hardness
Chromic Oxide, 85% Graphite, 15%	2	24,000	None	2	Pellets had good hardness

*PROPRIETARY INFORMATION

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(2) A high purity pellet of chromic oxide cannot be processed with available equipment, (3) Pellets produced by fuzing chromic oxide would probably have an unacceptable activity level due to the enameled surface produced by the slag effect of fuzing, and (4) Graphite blended with chromic oxide aids in the production of pellets which have desirable physical and thermal properties, but cannot be used because of the undesirable ballistic effects.

(6) Chromic Oxide Bonded to the Substrate by Phosphoric Acid (U)

*(U) Catalyst beds of chromic oxide bonded to stainless steel wire with phosphoric acid were fabricated of 12 x 12 mesh 305 stainless steel screen with a wire diameter of 0.025 inch. This was used as the substrate for this catalyst system. The screen was then spray coated with 85 percent orthophosphoric acid (H_3PO_4) and chromium oxide.

(7) Chromium Oxide Foamed in a Honeycomb Structure (U)

*(U) Hastelloy honeycomb material 0.125 inch thick with a cell diameter of 0.063 inch and membrane thickness of 0.005 inch was used for the substrate material. A mixture of chromium oxide and graphite powder was made to yield a desired porosity. The composite powder was compression molded into the honeycomb cells and baked in a furnace. Baking caused the graphite to decompose causing a foaming action which left a porous chromic oxide structure within the honeycomb cell.

(8) Electrophoretic Deposition of Chromic Oxide on Stainless Steel Screen (U)

*(U) The electrophoretic deposition technique for applying chromic oxide to the stainless steel screen was developed by the Georgia Institute of Technology. The 304 stainless steel screen structure was suspended in a bath of a colloidal suspension

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of chromic oxide in a metal salt solution. An electric field is effected between the suspended screen and the nickel salt solution. The charged chromic oxide particles move to the screen and the particle charges are neutralized and bonded to the wire screen.

(9)   Chromic Oxide Deposited on Dynapore Wire Laminate (U)

*(U) Catalyst beds of chromic oxide deposited on a laminated wire were fabricated. The structures are formed by spot weld fuzing several laminates of stainless steel together into a monostructure.

(U) Dynaport laminates used for catalysts beds were fabricated from 304 stainless steel material. The samples were chemically etched.

*(U) The etched samples were degreased and baked to remove contaminates, and immersed in a boiling saturated solution of ammonium dichromate in distilled water. The Dynapore laminate was then baked which causes decomposition of the ammonium dichromate to produce chromic oxide.

d.   Stability Tests (U)

(1)   General (U)

*(U) The objective of the stability tests was to verify adherence of chromic oxide to the substrate material. Three types of stability tests were performed: (1) Catalyst bend tests, (2) Thermal cycling, and (3) Physical shock. Presented in these paragraphs is a summary of these results; for more detailed results see Reference (12), "Catalyst Development for the Demand Gas Generator".

(2)   Test Description (U)

(a)   Catalyst Bend Tests (U)

(U) The bend tests consisted of bending samples

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of the catalyst material over a two-inch diameter
cylindrical bar and then straightening them back to
their original condition. Three samples of each candidate
were tested.

(U) Test evaluation consisted of visual examination
of the sample before and after test and recording changes
in the catalyst bond to the substrate.

(b) Thermal Cycle Tests (U)

(U) In order to determine the compatability of the
linear thermal coefficients of expansion of the catalyst
and the substrate, samples of each candidate system were
thermally cycled twice between $2100^{\circ}F$ and $70^{\circ}F$.

(U) Test evaluation consisted of visual examination
of the samples before and after test and recording any
changes in appearance.

(c) Physical Shock Tests (U)

*(U) The physical shock tests were devised for the
purpose of physically impacting the catalyst bed in an
attempt to dislodge the chromic oxide. Samples of the
candidate catalyst were affixed to a wood block. Another
wood block and the one with the catalyst attached were
held 1/2-inch apart with the catalyst toward the impact
surface. The blocks were then manually impacted to-
gether 200 times.

*(U) Evaluation consisted of a visual examination
of the sample catalyst beds and recording any dislodged
chromic oxide.

(3) Test Results (U)

(U) The results of the stability tests are shown in Table
XLII, and a numeric grading system was used to

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TABLE XLIII

BEND, THERMAL, AND PHYSICAL SHOCK TESTS (U)

(Three Samples Each)

	Bend Tests				Thermal Tests				Physical Tests			
	Flaking	Rubs Off	Bare Spots	Cracking	Flaking	Distortion	Bare Spots	Cracking	Flaking	Bare Spots	Cracking	Other
Standard Catalyst	1	1	0	0	2	0	2	0	1	0	0	0
Phosphoric Acid Bonded Chromic Acid	1	0	2	1	4	0	4	4	2	2	1	0
Oxidation of Nichrome Screen	0	1	1	1	0	2	1	1	1	1	0	0
Oxidation of Chromium Screen	1	0	1	0	1	0	1	0	1	1	0	0
Plasma Sprayed Chromic Oxide	1	0	0	0	0	0	0	0	0	0	0	0
Dynapore Laminate with Chromic Oxide	Not Applicable				1	0	1	0	1	1	0	0
Electrophoretic Deposition of Chromic Oxide	0	0	0	0	0	0	0	0	1	0	0	0
Chromic Oxide Foamed in Honeycomb	Not Applicable				1*	0	1*	4	1*	1*	0	0

LEGEND:
No noticeable occurrence - 0
Slight occurrence - 1
Medium occurrence - 2
Heavy occurrence - 3
Very heavy occurrence - 4

* Flaking and bare spots apparent on edges only.

signify the relative degree of each observed property. The results are also discussed below:

(a)   Standard Catalyst (U)

- *(U) Bend tests: There was a small amount of flaking and a small amount of green chromic oxide could be rubbed off, but no bare spots or cracking could be found visually.
- (U) Thermal tests: Some flaking was observed.
- *(U) Physical shock tests: Minor flaking was observed, but the particles were very small and were probably excess chromic oxide which was not removed by the compressed dry air cleaning.

(b)   Chromic Oxide Plasma Sprayed *(U)

- *(U) Bend tests: There were no cracks or bare spots and excess chromic oxide could not be rubbed off. There was a very small amount of flaking.
- *(U) Thermal tests: There was no observable flaking of the chromic oxide after the test.
- (U) Physical shock tests: There was no catalyst flaking or other noticeable deterioration as a result of these tests.

(c)   Oxidized Nichrome Screen (U)

- (U) Bend test: Cracking and small bare spots were observed after testing but there was no flaking. Fine particles of powder consistency could be rubbed off the screen.
- (U) Physical shock tests: A small amount of catalyst flaking which resulted in bare spots was observed after tests. There was no catalyst cracking.

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(d) Chromium Plated Screen, Oxidized (U)

- *(U) Bend tests: There was some chromic oxide flaking which caused bare spots on the stainless steel screen, but the chromium plating remained intact. No catalyst material could be rubbed off.

- *(U) Thermal tests: There was a slight amount of chromic oxide flaking resulting from the tests but the chromium oxide remained intact.

- *(U) Physical shock tests: The only noticeable change was some small flaking of chromic oxide, but the chromic plating remained intact.

(e) Chromic Oxide, Phosphoric Acid Bonded*(U)

- *(U) Bend tests: A minor amount of chromic oxide flaking occurred resulting in bare spots on the screen however, chromic oxide could not be rubbed off.

- (U) Thermal tests: Most of the catalyst flaked off, baring large portions of the wire substrate.

- *(U) Physical shock tests: A moderate amount of chromic oxide flaking was noticed. No cracking was observed.

(f) Chromic Oxide in a Honeycomb Structure*(U)

- (U) Bend tests: It was not possible to subject the honeycomb bed to the established bend test because of the inherent rigidity of the material.

- *(U) Physical shock tests: A few small particles of chromic oxide were dislodged during the shock tests, but no cracking of the substrate or chromic oxide was observed.

(g) Electrophoretic Deposition of Chromic Oxide (U)

- *(U) Bend tests: There were no detectable cracks,

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flaking, bare spots or any chromic oxide which could be rubbed off.

- (U)Thermal tests: There was no observable change in the test panels resulting from thermal cycling tests.

- *(U) Physical shock tests: A few small flakes of chromic oxide were jarred loose from the catalyst bed. There was no cracking or flaking.

(h) Chromic Oxide on Dynaport Laminate *(U)

- (U) Bend tests: The bend tests were not conducted on these samples because the wire laminate structure is very rigid.

- *(U) Thermal tests: A small amount of chromic oxide flaking caused bare spots observed after tests and additional small amounts of catalyst could be dislodged if the samples were impacted on a hard surface. There was no cracking of the catalyst.

- *(U) Physical shock tests: A small amount of chromic oxide powder was dislodged by the shock tests.

(4) Discussion of Stability Test Results (U)

*(U) The results of the stability tests were reviewed to determine the three alternate catalyst systems that would be further evaluated in three inch gas generator tests and compared to the performance of the standard catalyst. The only two candidates which exhibited undesirable results as an effect of the stability tests were the chromic oxide phosphoric acid bonded and the chromic oxide in a honeycomb structure. The phosphoric acid bond system lost relatively large amounts of chromic oxide during thermal tests.

(U) A review of the data summarized in Table XLIII

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revealed that the other five candidate systems performed as well as or better than the standard catalyst. Before the decision was made on the selection, it was decided that an additional test would be performed. Since none of these catalyst systems had been exposed to R-500 propellant, a test was performed to determine the relative activity of each when heated for a set period of time and placed on the surface of a propellant grain. The test procedure is described in Table XLIV.

*(U) The catalyst bed assembly description and test results for each are given in Table XLV. These data indicate that the oxidized nichrome wire and oxidized chromium plated wire have the least activity of the five candidates tested.

<u>e.</u>   Catalyst Activity Tests (U)

(1)   General (U)   .

(U) The objective of the catalyst activity test was to determine the relative activity of alternate catalyst bed assemblies as compared to the standard catalyst system. The relative activity was determined by subjecting the catalyst bed assemblies to static testing in the three-inch diameter demand gas generator test motor.

*(U) In order to decrease the number of variables on the test series, all of the tests were performed with R-500 propellant grains conditioned at $70^{\circ}F$, all the R-500 propellant grains were pressed from one propellant batch, and the method of ignition for all of the three-inch diameter motor tests was standard. The igniter consisted of an ammonium nitrate-guanidine nitrate pressed wafer placed on the R-500 grain surface.

(U) Ignition in the three-inch motor was accomplished by heating the catalyst bed just prior to test assembly. After the motor was assembled, the hot catalyst bed was lowered onto

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TABLE XLIV - LABORATORY PROCEDURE
FOR ACTIVITY TESTS OF CANDIDATE CATALYST BEDS (U)

1. A ring stand with a ring support was positioned so that the ring
    support was approximately 3/4 inch above the flame tip of a
    Meaker burner.

2. The catalysts were fabricated to the established procedure for
    each and the samples assembled as described in Table V. The
    samples were all 3 x 3 inches square.

3. The catalyst bed was placed on the ring support and heated for
    2 minutes $\pm$ 5 seconds over the Meaker burner flame.

4. The hot catalyst is immediately placed on the surface of a pre-
    weighed R-500 propellant grain. The hot catalyst is left on the
    grain surface for 20 seconds or until propellant combustion stops.

5. The R-500 propellant grain weighed again and the consumed weight
    recorded.

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TABLE XLV. CATALYST BED ACTIVITY TEST RESULTS (U)

Catalyst Type	Assembly Description	R-500 Con-sumed Grams	Remarks
Standard	3 layers 12 x 12 mesh screens Held together with Nichrome wire	14.7	Operated for 20 seconds
Chromic Oxide Plasma Sprayed	3 layers 12 x 12 mesh screens Held together with Nichrome wire	6.8	Stopped burning at 11 seconds
Oxidized Nichrome Screen	3 layers 16 x 16 mesh screen Held together with Nichrome wire	2.0	Stopped burning at 5 seconds
Oxidized Chromium Plate Screen	3 layers 12 x 12 mesh screen Held together with Nichrome wire	3.9	Stopped burning at 4 seconds
Chromic Oxide Electrophoretic Deposited	3 layers 12 x 12 mesh screen Held together with Nichrome wire	10.5	Stopped burning at 15 seconds
Dynapore Laminate	0.140 thickness of Dynapore 401580	15.0	Operated for 20 seconds

the ignition wafer. These operations are described in detail in the test procedure, TEST-143, "Demand Gas Generator (DGG) Testing Standard, Three-Inch Generators".

(2) Sample Preparation (U)

(U) The catalyst beds were supported in the three-inch test motor by attaching the beds to the support structure with nichrome wire.

(a) Standard Catalyst (U)

(U) Coated 12 x 12 mesh screen of a 0.025-inch wire diameter was die stamp cut into 2.850 to 2.840 inch diameter surfaces. Three of these wafers were placed one upon the other so that the outside diameters and the pore openings were aligned.

(b) Plasma Sprayed Chromic Oxide *(U)

(U) Coated 12 x 64 mesh screen of a 0.023-inch diameter wire and 9 x 9-1/2 mesh screen of a 0.063-inch diameter wire. Assemblies consisted of two layers of the fine mesh and one layer of the course mesh materials; two layers of fine mesh were placed one upon the other with the 64 warp wire 90 degrees out of alignment. The 9 x 9-1/2 screen was placed on top of these two screens.

(U) The fine mesh material was toward the R-500 propellant grain surface.

(c) Electrophoretic Deposited Chromic Oxide *(U)

(U) Coated 12 x 64 mesh screen of 0.023-inch wire diameter and 12 x 12 mesh screen of 0.025-inch wire diameter were used to fabricate the electrophoretic deposition bed assemblies. The two layers of 12 x 64 mesh material were placed one upon the other with the 64 warp wires 90 degrees out of alignment. The 12 x 12

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material was placed on top of these two screens so that the 12 x 64 mesh material was toward the R-5_{00} propellant surface.

(d) Dynapore Laminate with Deposited Chromic Oxide *(U)

(U) Coated panels of 0.14_0 thick Dynaport 4_0158_0 were die stamp cut into 2,85_0 to 2,856 inch diameter discs.

(U) The laboratory activity tests performed on the candidate catalysts during the stability test evaluation did demonstrate an operational difference with the different catalysts. Therefore the test was continued and each catalyst bed used in these tests was evaluated prior to static test. The only change made was that the catalyst bed was left on the R-5_{00} grain for 6_0 seconds instead of 2_0 seconds. The weight of R-5_{00} propellant consumed was recorded in anticipation that a correlation could be established between these test results and three-inch motor static tests.

(U) The catalyst beds were also subjected to an evaluation to ascertain the relative air permeability of each to compare to the standard system. The detailed description of the best procedure is given in Appendix A. These tests were conducted prior to static tests and laboratory activity tests discussed above.

(3) Test Description (U)

(U) Complete data describing pertinent data for the propellant grains, igniter overlay grains, catalyst beds, and components used in each test assembly are given in Reference (12).

(U) Measured date from the tests include, (1) Chamber pressure as a function of time, (2) Flame temperature as a

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function of time, and (3) Burning rate in the presence of the catalyst.

(U) The tests of each catalyst were conducted at two different K_n values in order to gather data to establish a primary burn rate -pressure and K_n-pressure relationships for each.

(4) Discussion of Results (U)

(a) Standard Catalyst (U)

(U) The reduced date for the three-inch gas generator tests are presented in Table XLVI . The standard catalyst was tested at K_n values of 2_075 and 1333. The measured chamber pressures and burn rates are shown in Figure 64 . Also, in Figure 64 is the burn rate and K_n relationship established for the standard R-5_{00} propellant system.

(U) Three of the six data points agree very favorably with the characterization data and three data points do not. A review of the test data did not uncover any probable cause for the scatter.

(b) Plasma Sprayed Catalyst (U)

*(U) The plasma sprayed chromic oxide catalysts were tested at gas generator K_n values of 2_075 and 1333. Tests at the higher K_n produced pressures of approximately 8_{00} psia but at the lower K_n value, an equilibrium operating pressure was not established.

(U) The measured flame temperatures of the plasma catalyst are the same as those for the standard catalyst.

(c) Electrophoretic Deposited Chromic Oxide Catalyst*(U)

(U) The burn rates and chamber pressures mea-

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TABLE XLVI

REDUCED DATA FROM CATALYST ACTIVITY TESTS (U)

Test No.	Date Tested	Type of Catalyst	K_n	K_n Equilibrium Pressure (psia)	Burn Rate (in./sec)	Burn Rate P_c (psia)	Flame Temp. (°F)	Time to Ignition Rise (sec)
TR-164	12-4-70	Standard	2075	850	0.0817	745	1426	6.0
TR-165	12-4-70	Standard	2075	651	0.0630	672	1290	6.8
TR-167	12-4-70	Standard	2075	710	0.0672	745	1020	6.1
TR-171	12-4-70	Standard	1333	445	0.0606	460	1188	5.0
TR-172	12-4-70	Standard	1333	388	0.0525	405	1163	6.4
TR-173	12-4-70	Standard	1333	424	0.0591	437	1180	5.6
TR-161	12-4-70	Plasma	2075	788	0.0708	786	1220	27.8
TR-162	12-4-70	Plasma	2075	795	0.0794	790	1262	catalyst hung up
TR-163	12-4-70	Plasma	2075	826	0.0786	838	1270	28.8
TR-168	12-4-70	Plasma	1333	- - -*	0.0735	509	1056	slow rise
TR-169	12-4-70	Plasma	1333	- - -*	0.0857	638	1170	slow rise
TR-170	12-4-70	Plasma	1333	- - -*	0.0867	600	1256	slow rise
TR-234	12-11-70	Electrophoretic	1784	1100	0.105	1114	1182	28.9
TR-235	12-11-70	Electrophoretic	1784	1200	0.112	1202	1010	33.1
TR-236	12-11-70	Electrophoretic	1784	1150	0.108	1124	1203	33.5
TR-237	12-11-70	Electrophoretic	1784	1230	0.118	1238	1182	35.2
TR-238	12-11-70	Electrophoretic	1784	1255	0.117	1233	1062	23.5
TR-257	12-14-70	Electrophoretic	1333	- - -*	0.119	1041	- - -	21.0
TR-188	12-8-70	Dynapore	1784	- - -*	- - -	- - -	684	6.3
TR-189	12-8-70	Dynapore	1784	- - -*	0.0312	301	812	4.4
TR-190	12-8-70	Dynapore	1784	790	0.0895	789	1000	2.7
TR-191	12-8-70	Dynapore	857	153	0.0357	153	800	14.7
TR-192	12-8-70	Dynapore	857	213	0.0452	218	820	37.9
TR-193	12-8-70	Dynapore	857	87	0.0216	87	820	5.4

* Did not attain an equilibrium level.

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Figure 64.   Performance Data from Standard
Catalyst Bed Activity Tests (U)

Chamber Pressure (psia)

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sured on these were outside the characterization range. Five of the tests were conducted at a gas generator K_n of 1784 and one test at a K_n of 1333. The motor tested at the lower K_n did not establish an equilibrium pressure.

(U) The burn rate-pressure data were relatively consistent. The K_n-pressure data, however, indicate the electrophoretic deposited catalyst to be more active than the standard as the measured chamber pressures at the 1784 K_n.

(d)   Chromic Oxide Deposited on Dynapore Laminate*(U)

(U) The Dynapore laminate catalysts were tested at gas generator to K_n values of 1784 and 857. The measured pressures at the higher K_n are very scattered and the pressures at the low K_n are outside the range of R-500 characterization. The burn rate date, however, correlates well with the extended burn rate data from the R-500 characterization tests. The measured flame temperatures are approximately $310^{\circ}F$ lower than those measured for the other three catalysts.

*(U) Post-test examination of the Dynapore laminate revealed that large amounts of chromic oxide had been removed during the tests.

(5)   Summary of Results (U)

*(U) Of the three candidate catalyst systems which were tested and compared, only the electrophoretic deposited chromic oxide system demonstrated improved performance over the standard catalyst system.

*(U) The Dynapore laminate bed experienced excessive chromic oxide loss.

f.   Catalyst Surface Area Effects (U)

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(1) General (U)

(U) The objective of this test series was to ascertain if the ballistic performance of the Demand Gas Generator could be effected by varying the surface area of the chromic oxide catalyst of the three alternate catalyst systems and the standard catalyst system.

(U) The R-500 grains and ignition overlay grains were controlled as in the catalyst activity tests. An ignition method identical to that of the catalyst activity tests was used.

(2) Sample Preparation (U)

*(U) The chromic oxide catalyst was applied to the substrate materials of each candidate catalyst system in accordance with their process procedures.

(U) The surface areas of the beds were varied by changing the mesh size of the substrate screens, wire diameters, and the number of screens for all but the Dynapore laminate.

(a) Standard Catalyst (U)

(U) Six beds were constructed, four were three screen assemblies and two were two screen assemblies, mesh sizes varied from 9 x 9 1/2 to 12 x 64, wire diameters varied from 0.023 to 0.063 inch, and alternate configurations of screen stacking was used.

(b) Plasma Sprayed Chromic Oxide*(U)

(U) Six beds were fabricated, four were three screen assemblies and two were two screen assemblies, mesh sizes varied from 9 x 9 1/2, and 12 x 64 to 60 x 60, wire diameters varied from 0.011 inch to 0.063, and alternate configurations of screen stacking were used.

(c) Electrophoretic Deposited Chromic Oxide*(U)

(U) Six beds were fabricated, four were three

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screen assemblies and two were two screen assemblies, mesh sizes varied from 9 x 9 1/2 to 12 x 64, wire diameter varied from 0.023 to 0.063, and alternate configurations of screen stacking were used.

(d)   Dynapore Laminate Coated with Chromic Oxide*(C)

(U)   Two beds were 0.14_0 inch and two were 0.13_0 inch thicknesses of Dynaport 4_0158_0 laminate processed by the standard procedure, and two beds were 0.14 inch thick Dynapore with a longer acid etching during processing.

(3)   Surface Area Determinations (U)

(U) Surface area determinations were made on a model 21_{00} A Orr Surface Area Bore-Volume Analyzer.   The instrument uses gas at the temperature of liquid nitrogen to obtain data for the B. E. T. equation from Reference   12   to calculate the gas volume that would be required to cover the sample with a monomolecular layer.

(U) Surface area determinations were not performed on all of the catalyst coated screens used, but samples of each screen size used and each type of catalyst application were evaluated.

(U) The date for each of the materials tested are given in Table XLVII.

(U) In addition to the B. E. T. tests air permeability tests were performed on each test sample in accordance with test procedures described in Appendix   A .

(4)   Test Description (U)

(U) The catalyst surface area effects tests were performed exactly like the catalyst activity tests.   Components incorporated and pertinent data on grains and catalyst beds are given in Reference   12 .   Measured data on the tests include

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TABLE XLVII

CATALYST COATED SUBSTRATE SURFACE AREAS   (U)

Catalyst Application Method	Material Size	Surface Area, Square Meter per Gram
Standard	9 x 9-1/2 mesh 0.063 in. wire	0.1060
Standard	12 x 64 mesh 0.023 in. wire	0.4730
Standard	12 x 12 mesh 0.025 in. wire	0.1820
Plasma Sprayed	9 x 9-1/2 mesh 0.063 in. wire	0.0270
Plasma Sprayed	12 x 64 mesh 0.023 in. wire	0.0604
Plasma Sprayed	12 x 12 mesh 0.025 in. wire	0.0642
Plasma Sprayed	60 x 60 mesh 0.011 in. wire	0.0606
Electrophoretic Deposited	9 x 9-1/2 mesh 0.063 in. wire	0.0354
Electrophoretic Deposited	12 x 12 mesh 0.025 in. wire	0.0073
Electrophoretic Deposited	12 x 64 mesh 0.023 in. wire	0.0420
Deposited on Dynapore Laminate	0.140 in. thick 401580	0.1510
Deposited on Dynapore Laminate	0.130 in. thick 402210	0.0728

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(1) Chamber pressure as a function of time, (2) Chamber temperature as a function of time and (3) Propellant burn rate in the presence of the catalyst.

(U) Tests of each catalyst were conducted at one K_n except the plasma spray coated catalyst which was tested at two K_n values. One test of each type (surface area type) was made on a K_n of 1080, the K_n at which the standard catalyst was tested, and one test of each at a higher K_n.

(5) Discussion of Results (U)

(U) The reduced data from the catalyst surface area investigation static tests are shown in Table XLVIII.

(a) Discussion of Results (U)

(U) Burn rate and K_n data from the standard catalyst surface area variation tests are shown in Figure 65. These data show that burn rate increases with surface area. The K_n data is presented and is in agreement with the burn rate data. The amount of R-500 consumed increases as the catalyst bed surface area increases by the relation shown in Figure 66. The air permeability tests did not indicate a trend or correlation with the surface area changes. The time to ignition rise varied from 4.9 to 33.6 seconds with no trend or correlation. These times are on the average much longer than those of the standard catalyst.

(b) Plasma Sprayed Catalyst Beds (U)

(U) Reduced data in Table XLVIII shows a slight increase in activity with increasing surface area, but the increase was uncertain as the scatter measured in the activity test was greater than the trend shown in these surface area effects tests.

TABLE XLVII   Reduced Data from Catalyst Surface Effects Tests (U)

Test No.	Date Tested	Type Catalyst	K_n	K_n Equil Press (psia)	Burn Rate (in./sec)	Burn Rate P_c (psia)	Flame Temp °F	Ignition Rise Time (sec)
TR-144	12-3-70	Standard	1080	413	0.0760	421	1180	4.9
145	12-3-70	Standard	1080	480	0.0860	471	1167	33.6
146	12-3-70	Standard	1080	526	0.0970	527	1220	19.5
147	12-3-70	Standard	1080	386	0.0636	388	1196	20.1
148	12-3-70	Standard	1080	(1)	0.0895	488	1274	15.7
TR-150	12-3-70	Plasma	1784	500	0.0615	516	510	25.6
151	12-3-70	Plasma	1080	(1)	(2)	(2)	(2)	(2)
152	12-3-70	Plasma	1784	(1)	0.0952	800	610	18.2
154	12-3-70	Plasma	1080	(1)	(2)	(2)	(2)	(2)
155	12-3-70	Plasma	1784	735	0.0877	712	1100	24.8
156	12-3-70	Plasma	1080	(1)	(2)	(2)	(2)	(2)
TR-228	12-11-70	Electrophoretic	1784	(1)	0.1104	1180	1432	52.1
229	12-11-70	Electrophoretic	1784	1155	0.1087	1152	1427	31.5
230	12-11-70	Electrophoretic	1784	(1)	0.1134	1200	1312	16.5
231	12-11-70	Electrophoretic	1784	975	0.0934	975	1328	50.3
232	12-11-70	Electrophoretic	1784	(1)	0.0883	897	1260	---
233	12-11-70	Electrophoretic	1784	1230	0.1170	1215	1062	55.7
TR-197	12-8-70	Dynapore	1784	380	0.0493	400	804	17.5
216	12-10-70	Dynapore	1784	680	0.0639	430	1158	3.8
224	12-10-70	Dynapore	1784	375	0.0565	377	1163	2.8
225	12-11-70	Dynapore	1784	190	0.0207	200	766	5.3
226	12-11-70	Dynapore	1784	430	0.0667	696	1338	4.8
227	12-11-70	Dynapore	1784	580	0.0565	593	1193	6.7

(1) Did not establish equilibrium operation.

(2) Pressures were very low and the data measured was questionable.

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Figure 65 - Performance Data from Standard
Catalyst Bed Surface Effects Tests (U)

Data from R-500 Characterization

K_n data

r_b data tests 144 and 145

r_b data tests 146 and 147

r_b data tests 148 and 149

Burn Rate (in./sec)

LOGARITHMIC 2 x 3 CYCLE 46 7203
KEUFFEL & ESSER CO.

Chamber Pressure (psia)

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Figure 66.— R-500 Consumed as a Function of Catalyst Surface Area Standard Catalyst (L)

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(U) The measured flame temperatures of two of the three measured values are approximately 50% of that measured during activity tests above.

(c)   Electrophoretic Deposition Catalyst Beds (U)

(U) The change in surface area from 18.6 to 36.6 square feet did not effect the ballistic performance. The data did agree with the characterized burn rate curve extended to applicable pressures.

(d)   Dynapore Laminate Catalyst Beds (U)

(U) Changes in surface area from 32 to 92 square feet did show an increase in burning rate but at the higher surface area values the data were scattered.

(U) The times to ignition rise on three tests were comparable to the standard catalyst and earlier activity Dynapore tests.

(U) Flame temperatures ranged from $766^{o}F$ to $1338^{o}F$ and on the average were higher than those measured in catalyst activity tests and the majority of the data comparable to the basic standard catalyst.

*(U) The condition of the catalyst beds after test, in all cases, was relatively poor. Large areas of the Dynapore laminate were bare where the chromic oxide coating had been lost and the catalyst beds were distorted.

(6)   Summary of Results (U)

*(U) Large changes in the surface area of the standard catalyst system were obtained by changing the substrate screen sizes and the burn rate of the R-500 propellant was effected by these changes. The time to ignition rise was inversely effected. None of the other catalyst systems demonstrated a pronounced effect of surface area on ballistic performance.

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This is partly due to the fact that large surface area variations were not obtained with the other catalyst systems.

*(U.) The Dynapore laminate catalyst beds again experienced a heavy loss of chromic oxide.

g. Catalyst Durability (U)

(1) General (U)

(U) The objective of the catalyst durability tests was to determine the effects of long duration motor operation on the activity of the three candidate catalyst beds and the standard bed. Catalyst degradation with motor test duration was to be characterized by a ballistic performance decrease.

(U) The R-500 grain and ignition overlay grain were controlled as in the catalyst activity tests. An ignition method identical to that of the catalyst activity tests was used.

(2) Sample Preparation (U)

*(U) The three candidate systems were the plasma sprayed chromic oxide, the electrophoretic deposited chromic oxide and chromic oxide deposited on the Dynapore laminate. Bed assemblies were prepared in accordance with process procedures except for the Dynaport laminate. Due to the availability of material, it was necessary to substitute 0.013_0 thickness Dynapore for the 0.014_0 thickness previously used.

(U) Each catalyst bed was subjected to the laboratory 60 second activity test and the air permeability tests.

(3) Test Description (U)

(U) The R-500 propellant grains and the ignition overlay wafers were conditioned at $70^\circ F$ for all tests.

*(U) Three sequential tests were conducted with each candidate catalyst bed. The first test of each catalyst bed was conducted in the standard manner as described in Northrop

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Carolina, Inc. test procedure TEST-143, "Demand Gas Generator (DGG) Testing Standard, Three-Inch Generators." After the first test, the motor was disassembled as quickly as possible and a Meaker burner placed under the catalyst bed to keep it hot. After a new R-500 grain and overlay were placed in the motor chamber, the burner was removed and the motor reassembled for the second test. This procedure was repeated for the third test of each catalyst bed.

(U) The tests of each catalyst bed were made at one K_n value selected to give motor performance in a known range of burn rate-pressure data and give the longest burn times.

(U) The tests were performed exactly like the catalyst activity tests. Components incorporated and pertinent data on grains, and catalyst beds are given in Reference 12. Measured data were the same as previous tests.

(4) Discussion of Results (U)

(U) Reduced data for the three tests conducted on each of the Standard, Plasma, Electrophoretic, and Dynapore catalyst bed systems are presented in Table XLIX.

(a) Standard Catalyst (U)

(U) A decrease of burn rate of 5.8% was experienced after 60 seconds of operation and 22.7% reduction after 92 seconds of duration.

*(U) Post-test visual examination of the catalyst beds was made and the chromic oxide catalyst was in very good condition. No loss of catalyst was observed.

(b) Plasma Sprayed Catalyst Beds (U)

*(U) Reduced data for this system is shown in Table XLIX. The three data points fall in a very tight group which indicates no degradation of the catalyst

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TABLE XLIX - . Reduced Data from Catalyst Durability Tests (U)

Test No.	Date Tested	Type Catalyst	K_n	K_n Equil Press (psia)	Burn Rate (in./sec)	Burn Rate Press (psia)	Motor Duration (sec)	Flame Temp °F	Ignition Rise Time (sec)
TR-194	12-8-70	Standard	857	250	0.0553	240	30	937	14.7
195	12-8-70	Standard	857	224	0.0510	226	31	940	10.1
196	12-8-70	Standard	857	240	0.0458	240	31	964	10.5
TR-244	12-11-70	Plasma	1784	740	0.0760	740	19	1180	9.1
245	12-11-70	Plasma	1784	716	0.0769	746	20	1117	19.3
246	12-11-70	Plasma	1784	740	0.0777	750	20	1000	22.1
TR-240	12-11-70	Electrophoretic	1784	1235	0.1350	1216	13	1144	32.1
241	12-11-70	Electrophoretic	1784	930	0.0982	952	15	1117	9.4
242	12-11-70	Electrophoretic	1784	830	0.0908	908	17	1000	4.4
TR-217	12-10-70	Dynapore	1784	340	0.0493	354	38	1116	1.0
218	12-10-70	Dynapore	1784	(1)	--	---	0	---	---
219	12-10-70	Dynapore	1784	(2)	--	---	0	---	---

(1) Did not attain a significant pressure nor establish equilibrium operation

(2) Did not ignite

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activity after three tests and a total duration of 59 seconds.

*(U) Post-test examination of the bed was made and the condition of the chromic oxide was very good. No loss of chromic oxide was observed.

(c) Electrophoretic Deposited Catalyst Beds (U)

*(U) The reduced data from the durability tests of the electrophoretic deposited chromic oxide catalyst beds are given in Table XLIX . The test durations were 13, 15, and 17 seconds, thus after 13 seconds duration the catalyst activity decreased 22.7%. Further testing at longer durations of up to 45 seconds did not cause additional decreases in activity.

*(U) Post-test visual examination of the catalyst bed revealed no loss of the chromic oxide catalyst and no degradation.

(d) Dynapore Laminate Catalyst Beds (U)

(U) The reduced data for the durability tests of the Dynapore laminate with deposited chromic oxide is shown in Table XI IX .

(U) The Dynapore system operated as expected for the first test. The second test was not successful because the activity of the catalyst bed had reduced to such an extent that the chamber pressure produced was too low to measure reliably. No ignition was achieved in the third test.

*(U) Post-test examination of the catalyst bed showed about 20% of the chromic oxide had been removed from a badly distorted bed.

(5) Summary of Results (U)

*(U) The activity of the standard catalyst was degraded

22.7% after a motor operating duration of 92.0 seconds. The plasma sprayed chromic oxide system did not experience any degradation when tested for duration up to 59 seconds. The electrophoretic deposited chromic oxide catalyst bed experienced a 22.8% reduction in the first 13 seconds of test, but did not show further degradation when tested for a duration of 45 seconds. The Dyanpore laminate, with chromic oxide deposited, experiences severe activity loss after one test and will not perform in a subsequent test, due to loss of chromic oxide from the laminate substrate.

h. Conclusions (U)

*(U.) Chromic oxide pellets were found to be unsatisfactory for this application. The commercially available pellets would not withstand the thermal cycling and studies performed to find suitable additives to enhance pellet properties were fruitless.

*(U) The phosphoric acid bonded chromic oxide system and the chromic oxide in a honeycomb structure were eliminated after thermal testing. The phosphoric acid bonded system experienced excessive flaking of the chromic oxide coating. The honeycomb structure developed a crack which broke the web structure.

*(U) The electrophoretic deposited chromic oxide system was the only one of the three candidates extensively studied which demonstrated improved performance, and was comparable to the standard catalyst system, in the activity test series.

*(U) The plasma sprayed chromic oxide system performed approximately the same as the standard catalyst system. The data from the tests of the Dynapore laminate system were scattered and post-test examination revealed excessive chromic oxide loss.

*(U) The standard catalyst system demonstrated more performance response to catalyst surface area variations than the three

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alternate catalyst systems. The plasma sprayed system surface area variations caused some response, but not enough to segregate the surface area effect from characteristic data scatter. Variations of chromic oxide surface area in the electrophoretic deposited system did not cause any variation in ballistic performance. The chromic oxide in Dynapore laminate surface variations did not effect ballistic performance.

*(U) The standard catalyst system experiences a loss of catalyst activity as demonstrated by the durability tests. The electrophoretic system experienced a similar decrease in activity. The plasma sprayed chromic oxide catalyst system, however, experienced no activity degradation or decrease in generator performance during the durability tests. The Dynapore laminate system proved inferior to all the other systems as the loss of activity was so pronounced that the tests could not be completed.

*(U) The electrophoretic system and plasma sprayed system had approximately four to five times longer delays to ignition rise than a demand gas generator utilizing the standard catalyst.

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APPENDIX A

PERMEABILITY TEST PROCEDURE (U)

(U) ASTM Test Method E128-61 titled, "The Standard Method of Test for Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use," was used in determining the air permeability of catalyst beds to be used in the Demand Gas Generator System.

(U) ASTM Designation E128-61 defines permeability as the flow of air in cubic feet per minute per square centimeter of filter area per one centimeter of water pressure differential.

(U) Permeability in the commercial fields of filtration absorption and diffusion is generally expressed as cubic feet of air flow per square inch per minute at one psia for comparative purposes, the units of area and volume are converted to the English system.

1 inch of water	=	0.0361 psi
1 cubic foot	=	28.316 liters
Area measured (constant)	=	0.138 in.^{2}

(U) The permeability test was performed as follows: A test probe of known surface area which was connected to a flowmeter is held on the catalyst bed surface. Pressure regulated air was metered through the flowmeter, probe and catalyst bed.

(U) Thirty liters of air were permitted to flow through the catalyst bed. The air flow time was recorded and air pressure readings recorded during air flow and after probe removal.

The permeability was calculated by the following equation:

$$P = \frac{F_v}{A_o \, \Delta P}$$

Where P = permeability

  Fv = volumetric flow

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A_o = orifice area

ΔP = pressure difference

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13. ABSTRACT

(U) A nineteen-month technology program was performed by Northrop Carolina, Inc. to demonstrate the ability of a demand gas generator concept to vary mass flow at constant pressure and efficiently meet advanced post-boost propulsion system requirements. The program consisted of a parametric study and preliminary design of a demand gas generator for advanced post-boost propulsion applications, the characterization of a standard propellant and catalyst, the development of improved propellants and catalysts, the development of a pyrotechnic/overlay ignition system, the development of an electrical catalyst control system, and system demonstration in twelve-inch diameter gas generator motors. Ten twelve-inch diameter motor tests were conducted which demonstrated a throttling ratio as high as 38 to 1, a 430-second operation, a 28-pulse simulated post-boost propulsion duty cycle, and the capability of operation at three different pressure levels. All basic program objectives were achieved and the feasibility of the demand gas generator concept for post-boost propulsion application was demonstrated.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Solid Propellant						
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Catalyst Control System						
Demand Gas Generator						
Mass Flow Variance						